REGIONAL HYRDROLOGIC CONTROLS ON ACID-SENSITIVITY OF LAKES IN BOREAL CANADA: AN ISOTOPIC PERSPECTIVE

by

KATRINA ELEANOR BENNETT
B.Sc., University of Victoria, 2000

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Abstract

This study applied the use of a stable isotope mass-balance model to calculate water throughflow, residency and water-yield and to assess acid-sensitivity for 50 lakes in the Athabasca Oil Sands region of northeastern Alberta. The research project was aimed at improving existing regional hydrologic estimates, based on coarse-scale runoff values derived from river gauging stations. Regional isotopic variations measured for components of the water cycle indicated a wide range of hydrologic conditions prevail, from throughflow, high water-yield lakes (186 $mm \cdot yr^{-1}$) to evaporative, low water-yield systems (23 $mm \cdot yr^{-1}$). Notably, hydrology is shown to be a controlling factor on acid-sensitivity and may be altering acid-sensitivity via such processes as water flow through peatland dominated catchments or convergence with acidic neutralizing soils, geology or ground waters. At the throughflow end of the hydrologic spectrum at low levels of isotopic enrichment, isotopes in precipitation were sensitive up to 30%. Relative humidity, on the other hand, is sensitive at high levels of enrichment at the evaporative end of the scale on the order of 25%.

This application, in conjunction with landscape and chemical analysis, highlighted the over-riding hydrologic processes occurring at lowland and upland systems of the Boreal Plain that may lead to increased acid-sensitivity or buffering capacity. This thesis documents the first ever demonstration of an isotope mass-balance model to estimate water-yields and subsequently assess critical acid loadings in North America. The results of this research project will allow for improved predictive ability and management of acid-sensitive aquatic ecosystems within future planning frameworks.

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Dedication

For my parents, Jim and Joan Bennett, sister Sarah, and my nephew Bennett Moyer.
Many thanks for the encouragement and love you have given me.

Epigraph

Dark Pines Under Water

This land like a mirror turns you inward
And you become a forest in a furtive lake;
The dark pines of your mind reach downward,
You dream in the green of your time,
Your memory is a row of sinking pines.

Explorer, you tell yourself this is not what you came for
Although it is good here, and green.
You had meant to move with a kind of largeness,
You had planned a heavy grace, an anguished dream.

But the dark pines of your mind dip deeper
And you are sinking, sinking, sleeper
In an elementary world;
There is something down there and you want it told.

~Gwendolyn MacEwen

Preface

This thesis is written as a series of stand-alone manuscripts designed to explore complementary aspects of Boreal Plains hydrology and their impact on acid-sensitivity of lakes in the Oil Sands region of Northeastern Alberta. The study is based on field work and modelling conducted during the course of the thesis, and has been funded by grants to J. Gibson from the Cumulative Environmental Management Association, an non-governmental organization (NGO) representing government, native groups, and some 50 industrial partners, including the major oil sands companies. Related support for this thesis project was also obtained via an NSERC Industrial Research Fellowship sponsored by Syncrude Ltd. This preface outlines the study and presents in brief the historical background to the research objectives, with special attention to the rationale and context.

The first contribution (Chapter 1) describes application and optimization of a stable isotope mass-balance approach for quantifying the hydrology of lakes and their contributing watersheds. Although technically challenging, the isotope mass-balance work is included at the outset of the thesis as it provides the essential quantitative basis for analysis of landscape controls on hydrology and linkages between regional lake water chemistry (Chapter 2), and the highlight of the project, which is a lake-specific critical acid loadings assessment and inter-comparison using isotope-based estimates of the hydrological fluxes (Chapter 3).

This thesis addresses a research problem related to the Athabasca Oil Sands, the largest recoverable oil sand development in Canada. Improved extraction techniques have allowed for increased production in the oil sands region, which is projected to rise from 964 thousands barrels per day (2003) to an estimated 3 million barrels per day by 2015 (ARD-AE 2004). This growth has ensured that the Athabasca Region of NE Alberta will be a major oil supplier to global markets for the next 50 years, second only to Saudi Arabia, and has fixed both the region and the province of Alberta at the top of the Canadian economic ladder for oil industry and production. Concurrent escalation of alternate pressures occurring within the area including gas exploration, forestry, urbanization, and industrialization has set the stage for mounting concern regarding environmental management in the region. Specifically, the release of NOx and SO_2 emissions associated with the mining and upgrading of bitumen has garnered attention regarding the aquatic freshwater ecosystems in the Athabasca Oil Sands area. To properly manage the potential effect of rising acid emissions on aquatic features, an understanding of current acid loadings to lakes and wetlands is vital.

This project aims to improve estimates of the baseline level of acidity in the region and provide the foundation for future modelling and analysis given the projected increases in production. Early investigations on acid-sensitive lake systems in Alberta began in the early 1980s to collect information from lakes where a potential issue was perceived (Erickson 1987, Saffran and Trew 1996). Various research groups to examine acid-sensitive lakes in the region carried out additional work during the late 1990s. Results from early studies and research programs were subsequently compiled into a 450-lake regional lake database, which was analysed in a working report published by WRS (2004).

A multi-stakeholder NGO called the Cumulative Environmental Management Association (CEMA) was established in 1997 to carry out the management of environmental issues and cumulative effects in the oil sands region identified under a Regional Sustainable Development Strategy (RSDS, AE 1999). In 1999, the Acid Sensitive Lakes program was established under the Regional Aquatics Monitoring Program (RAMP), also a directive of the RSDS, to begin monitoring at 50 lakes identified as acid-sensitive within the 450 lake data base. Thus, the work carried out at acid-sensitive lakes, as described in this thesis, is managed under the banner of CEMA, and carried out via RAMP. As noted above, funding for this research was provided by CEMA.

An underlining theme of this study is the goal of identifying and developing an understanding of acid-sensitive systems within western Canada's Boreal Plains. Alberta Environmental Protection (AEP) recognized the limitations of traditional approaches to management of acid depositions (based on target loadings) in this region (AEP 1990, CASA 1996). The Clean Air Strategic Alliance (CASA) thus established the Target Loading Subgroup, who recommended a critical acid load approach to management of acid emissions on soils and aquatic features (CASA 1996). The first application of critical loading in the region was completed for the 450 lakes using the Henriksen steady-state water chemistry (SSWC) model (WRS 2004). A key input parameter for the SSWC model is the annual catchment water-yield.

However, the prediction of water-yield of lake systems for this initial assessment was problematic. The methods used to determine catchment water-yield applied regional runoff values calculated using the Water Survey of Canada gauging stations. This approach to water balance measurement was noted to be inaccurate at the spatial scale of the monitored catchments (see Fig. 1.1). Thus, an improved technique using a stable-water isotope mass-balance model to capture the variability of water resources at an appropriate scale in the area was presented to CEMA. This tool would improve the spatial accuracy of the hydrology network, using the RAMP lakes as an initial test case. Thus, in 2001, the isotope component of the research was added to RAMP lakes project to estimate water balance in the lake systems. In 2004, a seasonal component was added, collecting monitoring information, isotopes and water chemistry to complement the annual sampling routine ongoing at the 50 RAMP lakes.

This research project was developed to provide a first approximation of the hydrologic fluxes at the RAMP lakes sites. Although the approach is a considerable improvement over the previous assessment, there are clearly limitations present in the research. These pertain to the lack of information at the catchment scale and the use of downscaled gridded climate data to estimate climate variables, such as relative humidity. There is a need for further refinement of the tool. This body of work represents only the first stage in development of a knowledge base pertaining to hydrologic interactions at the lake sites on a regional level, and the impact of these exchanges within the physical, climate and chemical mosaic present across the study area. Further refinements of the tool may result in new findings related to acid-sensitive systems and their management. Therefore the link between this research and acid-sensitivity should retain the research scope when considering the use of this application to further analysis.

The first component of this research addresses the isotopic approach to estimating water balance as applied in this study and is focused on in Chapter 1. This chapter aims to identify the issue at hand and provide the justification for the use of this tool to measure water balance on the Boreal Plain. Thus, the chapter begins with an explanation of the theory applied and derivation of isotope mass-balance model parameters and variables.

The study site is outlined, with reference to the overall climate and physical patterns present across the region. Following this, methods are outlined. Methodology largely pertains to the derivation of the isotope mass-balance model. A summary table was developed to include the source of information for each factor in the isotope model (Table 1.3). Finally, results and discussion present the findings as related to: the isotope model development, model testing and sensitivity analysis, and model output. Specifically, findings are discussed in the context of the Boreal Plain and the implications within this setting of the derived hydrologic parameters as measured by the isotope mass-balance water budget model.

Chapter 2 of this thesis presents the results of analysis using the isotope-based hydrologic estimates of the water balance generated in Chapter 1. The main objective was to apply a regional analysis of the interactions between hydrology, landscape and water chemistry at lakes located on the Boreal Plain. For this section of the work, only 40 lakes on the Boreal Plain have been described and examined. This narrowing of the data population allowed for more directed study of the relationships on the Boreal Plains without the influence of vastly different physical features found at excluded sites. Additionally, very little data was available at these sites.

Although much is still unknown about the hydrology in this region, Chapter 2 attempts to briefly examine the over-riding processes at work in this landscape. The theory of the isotopic mass-balance modelling tool is presented in this chapter only in summary, not in detailed form as found in Chapter 1. A description of the field sites, with details pertaining to surficial and bedrock geology, soils, forest cover and climate is provided. Both Chapter 1 and Chapter 2 contain details of the three years of study in terms of long-term climate signals and the variations in annual weather patterns experienced on a year-to-year basis during the span of the research. Also included is a discussion outlining the basis for selection of the 2003 chemistry data for data analysis, which ties the results of yearly and seasonal fluxes observed in temperature, precipitation and runoff together to justify the selection of this year for statistical measures.

Following this, methods are outlined for statistical analysis, detailed methodology is outlined in Chapter 1 pertaining to field sampling, and physical and climate data collection and processing. Results and discussion highlight the use of correlation statistics and multi linear regression to assess regional relationships. Results are provided for both water-yield and chemistry in relation to landscape interaction effects. The implication of these finding in the context of acid-sensitivity is provided in the summary of this work.

Chapter 3 presents the application of the improved water-yield calculations at lake sites in the context of critical acid loading models. Two methods of water-yield and critical loadings assessments are presented (Fig. 1.1), the first of which uses Water Survey of Canada gauges to assess water-yields and the second of which applies the use of the isotope mass-balance model to estimate water-yields at lake sites. The theory of isotope mass-balance modelling is addressed in this section, along with data collection and methodology employed for both approaches. Results are presented in terms of both the physical features of the catchments under study, and the results from water-yield estimates. The water-yields and critical loadings from both the isotope mass-balance model and the previous assessment are compared and contrasted with specific attention to illustrating where the two methods were successful. A discussion follows focusing on how the two water-yield and subsequent critical acid loading approaches differ in the region and for each specific study area. Implications and future directions for the research conclude this chapter, with discussion on the relevancy of fine-tuning of the water-yield calculation in the context of improved critical loadings assessments. The management implications of improved baseline estimates for acid-sensitivity of freshwater aquatic are addressed.

As a whole, the thesis provides an intensive look at recent progress made in application of an emerging isotope technique for water resources research in a complex, poorly understood and under-monitored region of Canada. Although targeted research, the work has contributed significantly to improving a methodology that may have wider applicability for study of hydrological processes, particularly for bridging the gap between water quantity and water quality research. It also offers new insight into the causes of hydrological variability across the Boreal Plain.

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Chapter 1 : The stable isotope mass-balance method: toward improved models for assessing regional hydrological variability on the Boreal Plain

Abstract

A stable isotope mass-balance method for estimating the water budget of lakes was applied and tested in order to assess model uncertainties and assumptions, and ultimately to improve capacity for regional application on the Boreal Plain of Alberta. Water sampling for stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ was conducted each September for three years from a network of 50 lakes across the oil sands region of northern Alberta, with a subset of lakes sampled on a monthly basis to provide insight into seasonal isotope cycles. Isotopic enrichment of the lakes beyond background concentrations was established from precipitation and groundwater databases and through supplementary sampling of precipitation and groundwater in the watersheds. These data were used in conjunction with climatic data and physical properties of the watersheds to establish throughflow, water residence times and water-yield from the catchment areas. A variety of isotopic models that applied different assumptions, as well as a range of climatic data sets were tested, and results are presented here. In general, the analysis reveals that the models are robust in nature and can withstand variations in input data across ranges of isotopic signatures found within the regional area from –16‰ and –7.5‰, and a wide range of variation in terms of input climate variables. At the throughflow end of the hydrologic spectrum at low levels of isotopic enrichment, isotopes in precipitation were sensitive up to 30%. Relative humidity, on the other hand, is sensitive at high levels of enrichment at the evaporative end of the scale on the order of 25%. Relative humidity was the only sensitive climate variable in the final version of the model; errors in estimation of relative humidity of approximately 20% will affect model output in terms of E/I ratios. This improved view of the sensitivity of the isotope mass-balance approach provides new perspective on the methods and use of this tool for water balance assessment and application on the Boreal Plains region of northeastern Alberta.

I. Introduction

Stable isotope mass-balance methods have been widely applied to the study of water budgets for individual lakes (Darling *et al.* 2005, Dincer 1968, Edwards *et al.* 2004, Krabbenhoft 1990, Yehdegho *et al.* 1997, Zuber 1983). Stable isotopes are useful for establishing the water budget of lakes as they are contained within the water molecule, have systematic distribution in precipitation and undergo evaporative enrichment due to kinetic fractionation during diffusion through the atmospheric boundary layer (Gat 1996). In the context of isotope mass-balance analysis, often employing the 1-D diffusion model of Craig and Gordon (1965), the enrichment can be used to constrain the additions/losses of water to/from individual systems. With notable exceptions (Gibson and Edwards 2002, Gibson *et al.* 2002, Prepas *et al.* 2001), relatively few studies have utilized isotope mass-balance of lakes for regional water balance assessment including variations in throughflow, water residence times, and water-yield from lake catchment.

In the Boreal Plains region of Northern Alberta there is considerable motivation for developing the capability for regional application due to extensive natural resource development and associated potential for environmental degradation across the region, as well as anticipated climate change impacts (Smerdon *et al.* 2005). One of the key issues, complicated by the limitations of the existing hydrometric network (Fig. 1.1), is the acid-sensitivity of lakes to NOx - SOx emissions from the oil sands refining operations centred in the Fort McMurray region (Saffran and Trew 1996). Application of conventional water and energy budget techniques (e.g., Lafleur *et al.* 1997, Moore *et al.* 2000, Parkhurst *et al.* 1998, Rouse *et al.* 1992, Rouse *et al.* 1977, Winter 1981; see also UNESCO 1981) to concurrently assess water balance of multiple lake catchments is often logistically complicated and costly, and is not well-supported by the Water Survey of Canada (WSC) gauging network, which is aimed primarily at capturing hydrologic flow within large river drainage basins (Fig. 1.1). The WSC stations were never designed to address the complexity of water balance, do not meet the needs of spatially broad research problems and are generally ill suited for downscaling to the headwater catchment level.

Due to complex, wetland-rich terrain and low topographic gradients, use of hydrological modelling in the region has tended to focus on highly permeable subsystems (e.g., Smerdon *et al.* 2005) or upland locations with higher than average relief (Evans *et al.* 2000). The primary difficulty has been in defining catchment boundaries and drainage features in areas where little topographic relief exists (see Pietroniro *et al.* 1996). The Canadian Boreal Plain exhibits very low topographic relief, due to geological influence and subsequent water-induced erosion controlling northern landscapes (Bachu 1999). The broad spatial extent of emissions, the limitations on use of hydrometric networks at the headwater scale, and complexity of terrain in this region prompted the application of alternate methods to calculate water balance measures in this study.

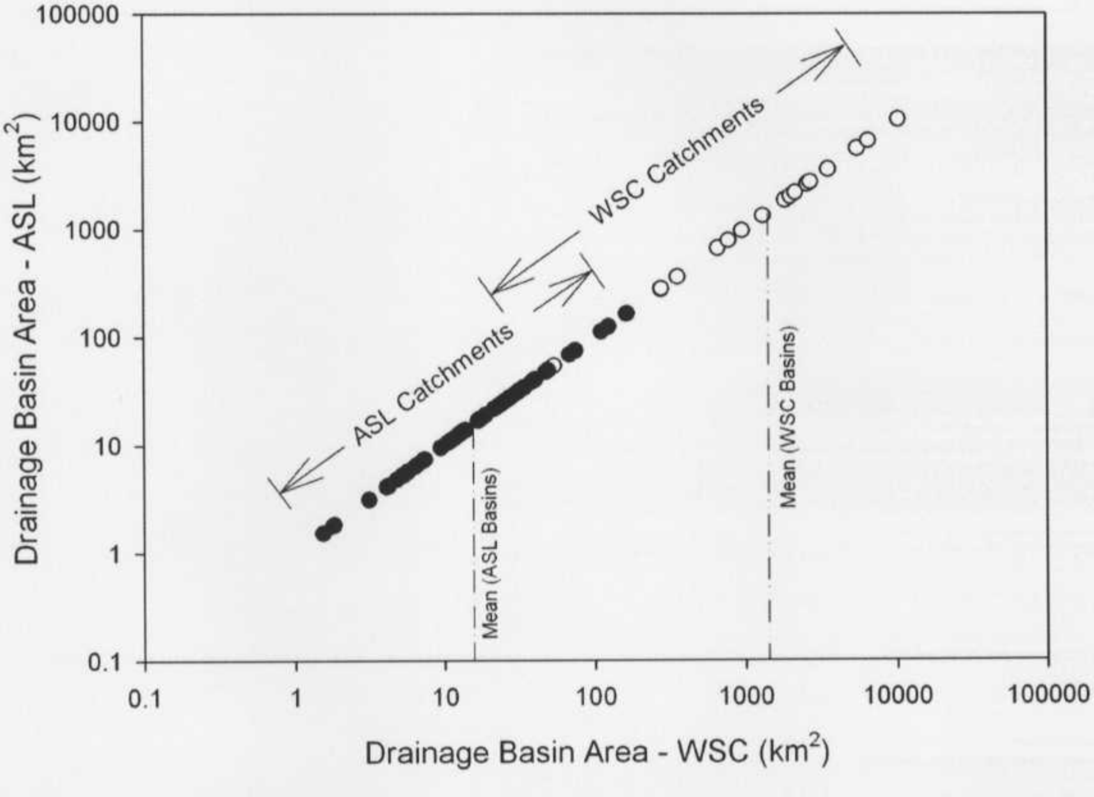


Figure 1.1 Scale of hydrometric network (WSC catchments) vs. scale of lake basins under investigation (ASL catchments). Note that the hydrometric network is focused on river basins several orders of magnitude larger than typical lake catchments across the oil sands region of northern Alberta. Dashed drop lines indicate the data population means, which illustrate the orders of magnitude difference between catchments analysed in this study (ASL) and WSC catchments. Arrows designate the upper and lower ranges of the ASL study catchments and WSC catchment data sets. For more detailed description and comparison of the two approaches to runoff calculation, see Chapter 3.

Better understanding of hydrological controls on the water quality and acid-sensitivity of lakes in the Boreal Plains region was the motivation for establishing an isotope-based assessment of water balance in 50 lakes under investigation by the Cumulative Environmental Management Agency (CEMA). The lakes were selected from among 450 lakes and ponds in Alberta originally sampled to assess acid-sensitivity during the late 1980's and monitored through the 1990s and in 2000 (Erickson 1987, RAMP 2004, Saffran and Trew 1996, WRS 2004). Alberta lakes are distinct from lakes in many other areas of Canada, and so have been recognized as requiring special, unique consideration for assessment of acid-sensitivity (AEP 1998). Differences include the high amount of peatland coverage in this region (Vitt and Chee 1990); the gentle rolling topography; geological properties of deep, loamy till formations with unique hydraulic conductivities (Ferone and Devito 2004, Hendry 1982); the predominance of small, shallow lake systems; a semi-arid climate (Winter 1989); and forest compositions that differ from other regions of the country (Prepas *et al.* 2001). One of the key recommendations of this body of work was to reassess runoff calculations, using stable isotope analysis, because the existing estimates were prone to error (Winter 1989, WRS 2004). Therefore, based on the results of this preliminary testing, a subset of 50 lakes prone to acid-sensitivity was selected for more in-depth analysis of runoff measures using stable isotope techniques.

This portion of the study (i.e., Chapter 1) aims to improve existing isotope-based modelling approaches for characterizing regional variations in water budget of lakes. The isotope approach is particularly effective as it uses evaporative enrichment of the isotopes oxygen-18 (^{18}O) and deuterium (^{2}H) in lakes as a kind of natural datalogger of hydrologic mechanisms and watershed functioning of their contributing landscape area. This approach has been previously applied with success. Further, is generally economical compared to conventional hydrological approaches and does not require intensive field measurements over broad temporal or spatial scales. The logistical advantages of using water samples collected during routine lake sampling, with subsequent analysis by routine isotope ratio mass spectrometry (IRMS), and of using fairly readily obtainable physical and climate data and supplementary precipitation isotope measurements based on precipitation and/or groundwater databases such as the Isotope Hydrology Information System (ISOHIS) and the Global Network of Isotopes in Precipitation (GNIP), suggest that the technique is suitable for broad classification work, such as is demonstrated herein.

This study initially adopts isotope balance approaches used in previous studies (Gibson *et al.* 1993a, Gibson *et al.* 2002). Because of some of the limitations identified in these previous studies, including uncertainty related to estimating the isotopic composition of some water balance components, temporal weighting of fluxes, the use of selected climatic data sets, and assumptions used in the modelling framework, the emphasis in this analysis was placed on assessing a variety of potential approaches to allow for evaluation of their respective usefulness via sensitivity analysis. Sensitivity analysis is a good measure of errors that may occur in the isotope model as a result of either measurement error or incorrect estimations of hydrological or physical and climatic variables. Gibson *et al.* (1993a) demonstrate the use of this approach for evaluating selected uncertainties, including reservoir storage, isotopic composition of atmospheric moisture, and humidity, to determine their relative sensitivity and impact on the modelling results. They found that small variations (+/-5%) in the atmospheric moisture and humidity components would not cause large errors to water-balance estimations, particularly for moderate levels of enrichment. Knoller and Strauch (2002), however, show relative humidity to be the most sensitive model parameter, and results can be significantly altered by small variances in this parameter. A similar appraisal of the Craig-Gordon model (1965) used in this and other analogous assessments indicated that humidity can lead to high error propagation for extreme conditions (relative humidity > 0.8) (Kumar and Nachiappan 1999). This research project provides additional insight into the sensitivity of key model parameters, and in doing so helps to build a more complete picture of regional variations in water budget across distinctive subregions of northeastern Alberta.

The main objective of this chapter is to provide an estimate of water balance for remote, northern lake sites and to prove the applicability of an isotope mass-balance approach to assess water balance parameters for lake and ponds across this region (i.e., the Boreal Plain). Thus, this segment of the study meets the overall research objective of estimating acid-sensitive lakes in the Alberta Oil Sands region by providing the water mass-balance approximations necessary to complete this assessment. A large component of the introductory body of this work therefore focuses on the explanation of the theory applied in isotope mass-balance approach and derivation of model parameters and variables. A description of the study site outlines the research lakes and the general patterns of climate, vegetation, geology and soils observed. The methods section explains the data collection requirements of the isotope mass-balance model, including the annual and seasonal field monitoring, the physical, climate and isotopic data estimation and the procedures undertaken to adjust these factors (for example, evaporation flux weighting). Results and discussion are concatenated into a single section in this chapter. Each result from the isotope model data collection procedure is provided, including the annual and seasonal lake water isotopic data, isotopes in precipitation, groundwater data results and river water collection. Results from climate and physical extraction are presented and a discussion follows explaining the input of this data into successive isotope model development stages, from the most simple first approximation to the more advanced dual fit isotope mass-balance model that applies the techniques of flux-weighting theorized in Gibson (2002) and applied in this research. Following this, sensitivity analysis is discussed, including the three tests used to understand the possible range of input variants that could be used and how this may alter isotope model output. Model output is then presented in context of the Boreal Plain, with the intention of detailing the range of conditions found within the lake systems and to provide the background for the analysis undertaken in Chapter 2. A common theme through this research is the application of stable isotopic water mass-balance for the assessment of critical acid loading models. The result of this application is presented in Chapter 3.

II. Theory

Isotopes were applied to the estimation of water budgets for a 50-lake network using a steady-state isotopic mass-balance approach. This tool takes advantage of the natural labelling that occurs as a water parcel travels through the hydrologic cycle and is exposed to phase changes and diffusion, which systematically shifts the abundances of rare, heavy isotopic species of water ($^{1}H^{2}H^{16}O$ and $^{1}H^{1}H^{18}O$) in relation to those of the more common light isotopic species ($^{1}H^{1}H^{16}O$) (see Gat 1995, 1996). For the open-water season within a lake system operating at steady-state (Fig. 1.2), free-water evaporation will occur from the lake water surface, resulting in isotopic fractionation both due to equilibrium exchange and driven by vapour pressure effects, and kinetic fractionation due to effects produced by molecular diffusion in air (Merlivat and Jouzel 1979). To a first approximation, inflow waters (both surface and subsurface) and incoming precipitation retain their primary isotopic composition, and do not suffer the effects of fractionation (Fritz and Fontes 1980.). For ideal, well-mixed lakes, outflow waters will acquire an isotopic signal that is similar to the lake itself. Providing that the isotopic composition of components is distinct, evaporative enrichment is sufficient and lake residence time is long enough to allow build-up of heavy isotopes in the residual water, the model can be applied to the estimation of the water balance. The approach essentially becomes a non-linear two-point mixing model for evaporation loss, based on offset between the lake and precipitation toward the atmospheric limit on enrichment defined by the background isotopic composition of the atmosphere and the total fractionation (Fig. 1.3). More complex non-steady state models have been developed to account for short-term changes observed in more extreme snowmelt-driven climates (Gibson 2002b), although their use in the present study is generally shown to be unnecessary.

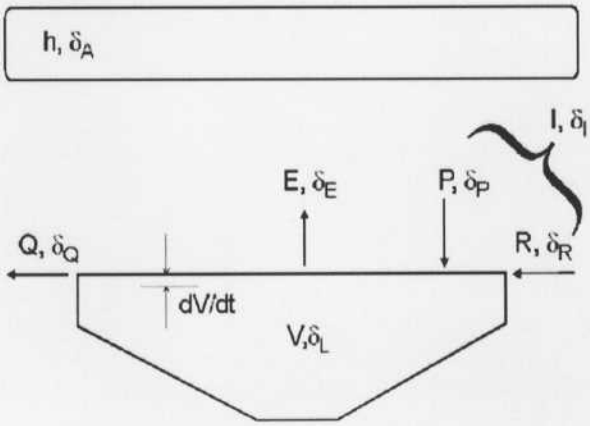


Figure 1.2 Schematic of lake showing water budget components and isotope compositions. Inputs into the systems are represented by inflow (I) and its isotopic composition (δ_I) and includes components of precipitation ($P\delta_P$) and runoff ($R\delta_R$). Outflow is represented by evaporation ($E\delta_E$) and discharge ($Q\delta_Q$). dV/dt is the change in volume over the change in time of the lake system. V is the volume of water in the lake and its isotopic composition (δ_L). The atmospheric isotopic component (δ_A) is represented by humidity (h). Figure from Gibson *et al.* (2002).

Evaporated waters (lake water) and source waters (precipitation and groundwater) are often clearly defined by different trends in $\delta^{18}O$ and δ^2H space (Fig. 1.3). Source waters generally fall along what is referred to here as the meteoric water line (MWL; Dansgaard 1964), which retains a slope 8 at the global scale (i.e., GMWL; $\delta^2H = 8\delta^{18}O + 10$; Craig 1961), with local lines (LMWL) deviating to slightly lower slopes as compared to the global pattern (see Fritz *et al.* 1987 for Canadian examples). These slight regional variations in the MWL from the global average arise from distinct histories of regional air masses, including evaporation sources, recycling ratios and secondary effects such as snow formation or evaporation from raindrops (Araguas-Araguas *et al.* 2000). Source waters will shift along the LMWL based on temperature effects related to seasonality and air mass origin (Dansgaard 1964, cited in Gibson *et al.* 1993a). Isotopic relationships for evaporated waters also are well defined by local evaporation lines (LEL), exhibiting slopes that usually fall between 4 and 6. Evaporated waters deviate from the input waters based on their hydrologic status across a range: from throughflow lake systems (influenced heavily by input source precipitation) that lie close to the intercept of the MWL and the LEL to evaporative systems (influenced by fractionation effects), which will occur at a distance away from the intercept position based on the relative amount of evaporation they have undergone. Evaporated waters found within headwater basins intersect the MWL at a point that closely reflects the source water input to the lakes, i.e., the mean isotopic composition of local precipitation (Gibson and Edwards 2002).

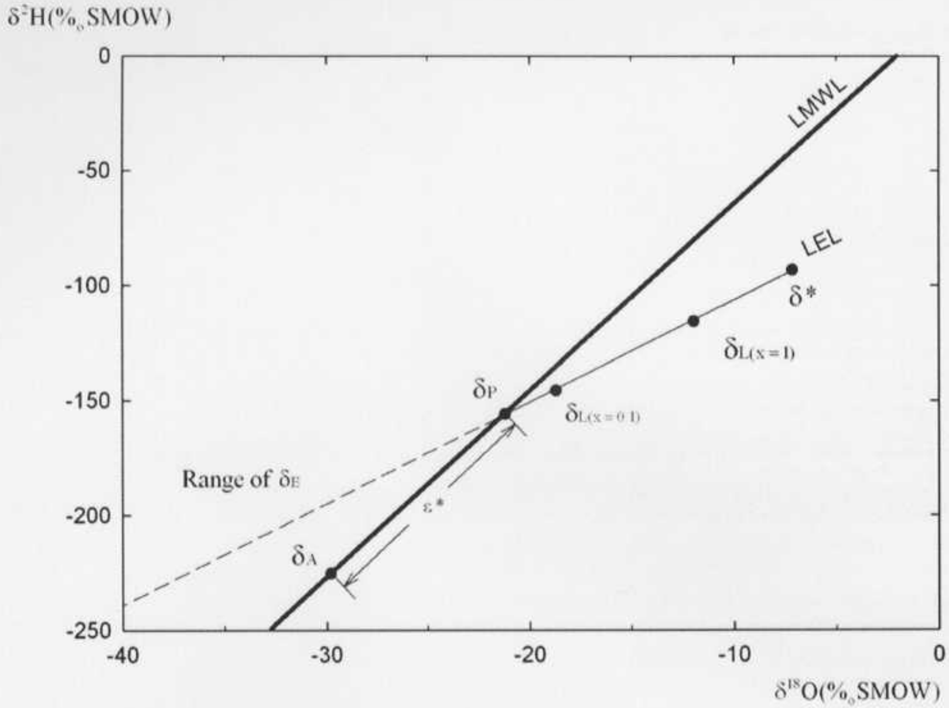


Figure 1.3 Generalized δ^{18}O versus δ^{2H} plot. See text below for details.

For evaporative systems, the classical picture portrayed by Gat (1996) and others (see also Gibson *et al.* 1993a) is that the offset of lake water from the MWL along the LEL is controlled by the limiting isotopic enrichment δ^* and the throughflow or flushing rate of the lake. Atmospheric moisture, δ_A, is normally depleted from δ_P by roughly ϵ^* and lies close to the MWL, which largely determines the LEL slope and gives rise to a depleted evaporation flux, δ_E, plotting along the extension of the LEL. The MWL in Fig. 1.3 is based on data from the Canadian stations of GNIP (CNIP), which is essentially a local meteoric water line for Canada (LMWL) based on 22 Canadian stations. There are actually 24 stations included in the entire CNIP database; however, the stations with three or less years of data (as of 2001) were not included (Inuvik and Pond Inlet, NWT).

Water and isotope balance of an ideal, constant-volume lake exposed to evaporation are given, respectively, by:

(1) $I_L = Q_L - E_L$,

and

$$(2)\ \mathrm{I_L}\delta_\mathrm{I} = \mathrm{Q_L}\delta_\mathrm{Q} - \mathrm{E_L}\delta_\mathrm{E},$$

where $\mathrm{I_L}$ is the lake inflow(s) and δ_I is the isotopic composition of inflow waters; $\mathrm{Q_L}$ is the lake outflow, with δ_Q being the isotopic composition of that outflow; and $\mathrm{E_L}$ is lake evaporation, with δ_E equalling the isotope composition of evaporated waters. In this equation, lake inflow and outflow are assumed to represent combined surface and subsurface flow. In a well-mixed lake system, the average isotopic signal for the lake can be assumed equal to the outflow value, such that $\delta_Q = \delta_L$. Additionally, the mean annual isotope signal in regional precipitation is equal to the isotopic signature of inflow water $\delta_I = \delta_P$. This regional input signal encompasses all source waters, and assumes that the shallow groundwater input into the system will be equal to the average input precipitation signal. The isotope mass-balance model as applied in this study does not specifically account for deep, regional groundwater inputs to the lakes.

The fraction of water loss by evaporation (*x*) is obtained by rearranging Eq. [1] and substituting Q = I – E into Eq. [2], such that:

$$(3)\ x = \frac{E_L}{I_L} = \frac{E_L}{E_L + Q_L} = \frac{\delta_P - \delta_L}{\delta_E - \delta_L},$$

The most difficult factor to determine in the isotope mass-balance equation is the isotopic value for evaporative flux, δ_E, because it cannot be directly measured in the field (Gat 1996, Gibson *et al.* 1993a). Therefore, estimates of evaporation must be derived on the basis of a 1-D diffusion model, initially proposed by Craig and Gordon 1965, which requires an estimate of temperature at which evaporation occurs, boundary layer state and ambient atmospheric conditions (Gibson and Edwards 2002). A simplified version of the original Craig and Gordon (1965) model is often used (Gat 1996):

$$(4)\ \delta_E = \frac{\alpha^{*-1}\delta_L - h\delta_a - \varepsilon}{1 - h + 10^{-3}\varepsilon_K},$$

where *h* is atmospheric relative humidity (expressed as a fraction 0 – 1, standardized to the temperature-dependent saturation vapour pressure at the liquid-vapour interface), α^* is the equilibrium liquid-vapour fractionation factor, and:

$$(5)\ \varepsilon = \varepsilon^* + \varepsilon_\mathrm{K},$$

where ϵ, ϵ^* and ϵ_K are total isotopic separation, and equilibrium and kinetic separation, respectively. The isotopic separation factors are influenced by differences in the molecular diffusion properties of water molecules at the boundary layer (Kendall and McDonnell 1998). ϵ^* can be predicted from equations derived via experimental laboratory tests and temperature data (Horita and Wesolowski 1994). δ_A is calculated by coupled scaling of the equilibrium isotopic separation values for oxygen and hydrogen (ϵ^*) to achieve a best-fit match to the slope of the regional ^{18}O-^{2}H evaporative enrichment trend, thereby accounting for seasonality effects (see Gibson 2002a). The boundary layer environment and humidity conditions (Gibson 2002a, Gonfiantini 1986) drive kinetic separation, ε_K:

$$(6)\ \varepsilon_K = C_K(1-h),$$

where C_K is estimated using constant values of 14.2 (oxygen) and 12.5 (hydrogen), which are appropriate estimates for evaporation in lake systems (Gibson 2000).

After substitution of δ_E from Eq. [4] into Eq. [3] and rearranging we obtain:

$$(7)\ x = \frac{(\delta_L - \delta_I)}{m(\delta^* - \delta_L)},$$

where δ_L represents the isotopic composition of the lake at steady state, *m* is the enrichment slope given by:

$$(8)\ m = \frac{h-\varepsilon}{1-h+\varepsilon_K},$$

and δ^* is the limiting isotopic enrichment under local atmospheric conditions (Gat and Gonfantini 1981):

$$(9)\ \delta^* = \frac{h\delta_A + \varepsilon}{h - \varepsilon \cdot 10^{-3}},$$

The isotope mass-balance model has been used in previous studies to estimate E/I (x) ratios, as well as to constrain lake residence times and water-yields (see Gibson *et al.* 2002). The (E/I) or *x* ratio is a measure of the hydrologic status of the lake system, and is independent of variables such as the climate and catchment features. Residence time (τ) is usefully calculated from the annual throughflow index (x), lake volume (V, m^3) and lake evaporation (E, m^3/yr) (Gibson *et al.*, 2002):

$$(10)\ \tau = \frac{xV}{E}(years),$$

Water-yield in this study is defined as the flow of water occurring over the net catchment area. Water-yield (Wy, m^3) to the lake may also be calculated by subtracting precipitation on the lake surface (P_L) from isotopically evaluated inflow to the lake, as:

$$(11)\ W_Y = \frac{E}{x} - P_L,$$

which may also be expressed as a depth equivalent (mm) or runoff ratio (mm/mm precipitation) by dividing by the net catchment area assuming this can be estimated accurately.

III. Site Description

The lakes under study are located in northeastern Alberta, Canada (55° 30' 110°W to 60°N 115° 30'W; Table 1.1, Fig. 1.4). The town of Fort McMurray is central to the study area, located at 56° 39' N and 111° 13' W; most of the major oil sands operations lie within a 100 km radius of Fort McMurray. Forty lakes are situated within 200 km of the town of Fort McMurray and its associated oil sand developments; outside this radius five lakes are found in the Caribou Mountains and five lakes are situated north of Lake Athabasca. The study watersheds are primarily headwater systems that range in size from shallow, small ponds (1m deep, < 0.5 km^2) to large lakes (30 m deep, 43 km^2), with average lake depth and size equal to 4.3 m, and 3 km^2, respectively. Average catchment areas are approximately 27 km^2 in size, with minimum catchment areas of 1.5 km^2 and maximum catchment areas of 164 km^2. The lakes were initially a component of exploratory work on acid-sensitive lakes in Alberta, and were selected for further study based on their water chemistry (RAMP 2004).

Table 1.1 Lake sites, locations and basic physical parameters. Latitude and longitude are given in decimal degrees (dd). DBA = drainage basin area. Sampling type defines whether lakes were sampled under either the annual or seasonal monitoring program.

Lake Number	*Region*	*Latitude (dd)*	*Longitude (dd)*	*Lake Area (km^2)*	*DBA (km^2)*	*Sampling Type*
NE1	REGION 1	57.15	-110.85	0.7	13.8	Annual
NE2	NE Fort McMurray	56.64	-110.20	4.2	31.9	Annual
NE3		57.29	-111.24	5.8	74.7	Annual
NE4		57.09	-110.75	0.3	17.3	Annual
NE5		57.05	-110.59	0.6	7.2	Annual

Lake Number	*Region*	*Latitude (dd)*	*Longitude (dd)*	*Lake Area (km^2)*	*DBA (km^2)*	*Sampling Type*
NE6		57.69	-110.40	1.2	17.1	Annual
NE7		56.89	-110.90	1.9	21.5	Seasonal
NE8		57.27	-110.90	0.4	11.1	Annual
NE9		57.15	-110.86	0.1	4.2	Seasonal
NE10		57.23	-110.75	0.1	6.6	Seasonal
NE11		56.77	-100.91	3.2	23.2	Annual
SM1	REGION 2	55.76	-110.76	2.4	9.5	Annual
SM2	Stony Mountains	56.26	-111.26	1.4	18.7	Annual
SM3		55.79	-111.83	2.0	26.3	Annual
SM4		56.20	-111.37	1.9	6.4	Annual
SM5		56.15	-111.23	0.5	12.5	Annual
SM6		56.17	-111.55	1.1	7.4	Annual
SM7		56.22	-111.17	0.7	4.1	Seasonal
SM8		55.68	-111.83	1.5	7.3	Seasonal
SM9		56.21	-111.20	1.9	11.6	Seasonal
SM10		56.22	-111.25	1.1	10.5	Annual
WF1	REGION 3	56.35	-113.18	3.2	27.4	Annual
WF2	West Fort McMurray	56.24	-113.14	0.8	24.1	Annual
WF3		55.91	-112.86	2.2	40.3	Annual
WF4		57.15	-111.98	0.0	1.8	Seasonal
WF5		56.80	-111.92	0.2	7.1	Annual
WF6		56.81	-111.72	0.2	5.3	Annual
WF7		56.78	-111.79	0.1	1.8	Annual
WF8		56.77	-111.95	2.0	29.1	Annual
BM1	REGION 4	57.41	-112.93	17.0	68.3	Annual
BM2	Birch Mountains	57.31	-112.40	0.4	5.5	Annual
BM3		57.69	-111.91	0.1	1.5	Annual
BM4		57.42	-112.69	44.0	163.6	Annual
BM5		57.65	-112.62	1.0	29.6	Annual
BM6		57.69	-112.74	4.3	38.4	Annual
BM7		57.76	-112.58	2.6	30.5	Seasonal
BM8		57.85	-112.97	1.3	19.7	Annual
BM9		58.06	-112.27	0.7	8.5	Annual
BM10		57.77	-112.40	1.2	33.9	Seasonal
BM11		57.70	-112.38	3.5	33.7	Seasonal
CM1	REGION 5	58.77	-115.44	1.6	25.5	Annual
CM2	Caribou Mountains	59.13	-115.13	9.6	47.5	Annual
CM3		59.19	-115.46	2.3	27.6	Annual
CM4		59.31	-115.35	2.6	38.4	Annual
CM5		59.24	-114.53	0.6	3.1	Annual
S1	REGION 6	59.72	110.02	3.4	16.8	Annual
S2	Shield Lakes	59.12	-110.83	1.0	111.3	Annual
S3		59.19	110.68	1.4	31.1	Annual
S4		59.17	-110.57	1.4	124.5	Annual
S5		59.13	110.69	0.3	4.8	Annual

Thirty-year (1971–2000) air temperature normals at Fort McMurray are 16.8° C in summer (July) and –18.8° C in winter (January) (MSC 2004). Mean annual and May-October (open-water season) values, along with annual average totals for precipitation and relative humidity (average) are given for all years of the study versus the 1971-2000 period as measured at the Fort McMurray climate station (Table 1.2). 2001 is included to represent the pre-year runoff contributions that may be antecedent moisture conditions affecting water availability from the previous season. The water year begins in May, when winter thaw and spring freshet initiate active hydrologic exchange between melt waters, lakes and rivers. Freeze-up starts during October, and lakes are ice-covered by November, at which time evaporation and other climate processes are effectively shut down. Mean annual precipitation is 456 mm, of which 74% falls as rain during the open water season period and the remainder falls as snow during winter months (MSC 2004). Average annual evaporation is 480 mm (Hamon 1961, New *et al.* 1999), and January relative humidity is 75%, while in July it is 70% (New *et al.* 1999).

Table 1.2 Climate data for the Fort McMurray climate station for the pre-season, and the 2002-2004 study years. Climate normals at this station are also given for the period of 1971-2000 (MSC 2004).

Year or Climatology	*Mean Annual Temp*	*Mean Open-Water Temp*	*Annual Total Precip*	*Relative Humidity*
2001 (pre-season)	2.1	11.9	359	N/A
2002	-0.3	10	422	N/A
2003	0.6	11.8	496	N/A
2004	-0.1	9.8	327	N/A
Fort McMurray 1971-2000	0.7	11.6	456	66.3

The lakes are grouped within six sub-regional study areas, namely, (1) Northeast Fort McMurray, (2) Stony Mountains, (3) West Fort McMurray, (4) Birch Mountains, (5) Caribou Mountains and (6) Shield Lakes; four of these sub-regions are considered to fall within a 200 km radius of Fort McMurray and the oil sands operations, in what is referred to here as the impacted zone for acid deposition (Shell 2005, see also Fig. 2.1). Two (control) groups are located outside this zone (to a maximum of 400 km); of these, one is located in the Caribou Mountains and the other in the Shield site north of Lake Athabasca.

Lakes are highly variable in their morphology, both within and between sub-regions; all lakes were formed via glacial processes. Lake systems may be small, shallow and round, and may have been formed by irregularities in glacial drift tills (Kalff 2002). Ice-scour lakes may be the primary lake type found in the Shield area; lakes in this region tend to be elongated, with multiple inflow arms. Lakes on the Stony Mountain and Birch

Mountain plateaus tend to be larger and tear-dropped in shape, occurring over morainal materials.

Study regions range in elevation from 200 m (Region 6) to 1000 m (Region 5), with similar average elevations occurring within Regions 1 and 3, and within Regions 2 and 4. The average slope for the data set is low (2.3%): individual catchments range in slope from 0.5% in Region 3 to 5.4% in Region 4. The lowest average slopes for regions are found in Regions 1 and 3 (1.2% and 1.3%), with slightly higher slopes occurring in Region 2 (1.8%). Higher average slopes occurring in Regions 4, 5 and 6 (2.9%, 2.9% and 3.9%, respectively).

The 50 lakes fall into three different ecozones as defined by the National Ecological Framework for Canada (Marshall and Schut 1999, Ecological Stratification Working Group 1996). The four regions near the oil sands operations (impacted) lie primarily within the Boreal Plain ecozone. The control sites lie within either the Taiga Plain (Caribou Mountains) or the Taiga Shield ecozones. Permafrost is sporadic discontinuous (10–50%) with low ground ice (<10%) at the Shield and Taiga Plain sites, and in the remainder of the sites permafrost is either not present or occurs as isolated patches (0–10%), with low or low-to-nil ground ice (Brown 1998).

Regional surficial materials consist primarily of thick tills (65%), till veneers (21%), with some coarse sands and silts (3%) and minor amounts of sands and gravel, fine silts and clay (Fulton 1996). Soils in Region 1, 2, 3 and 4 comprise Organics, Luvisols, Brunisols and Cryosols (Region 4), while Cryosols and Regosols are dominant soil types in Regions 5 and 6, respectively (Shields *et al.* 1991, SLCWG 2005).

Black spruce is the dominant cover type by area (53%) found within the 33 catchments analysed (data were not available for the entire 50 lake data set), with jack pine (12%), trembling aspen (8%), and tamarack (4%) as second, third and fourth most common, respectively. The overall study area comprises 13% bogs, 22% fens and 65% mineral upland; peatland coverage in specific watersheds varies, but the average amounts are very similar to statistics for the region at large (Vitt *et al.* 1996).

Ten lakes were selected for seasonal study during the summer of 2004. These ten lakes are found within Regions 1 through 4; no lakes from the Caribou Mountains or Shield lakes were selected for seasonal analysis. Lakes were selected on the basis of their representative size, hydrology and acid-sensitivity, in order to ensure that a representative sample was obtained across the low to high ranges of these factors. On average, lake drainage basin areas (15.7 km^2) for the seasonal lakes are smaller than the average system found within the entire 50-lake data set; the same is true for lake sizes (1.6 km^2) and maximum lake depths (2.3m). Slopes are generally lower in this data set compared to average values for all lakes, with low values of 1.6% and maximums of 23.2%. Average water-yields, residence times and runoff ratios are similar to those of Regions 1 and 2 (91 mm, 0.7 and 0.2, respectively). There is 8% bog, 31% fen and 60% upland in these catchments; this is slightly less bog and more fen than found in the 50-lake catchment data set (Vitt *et al.* 1996).

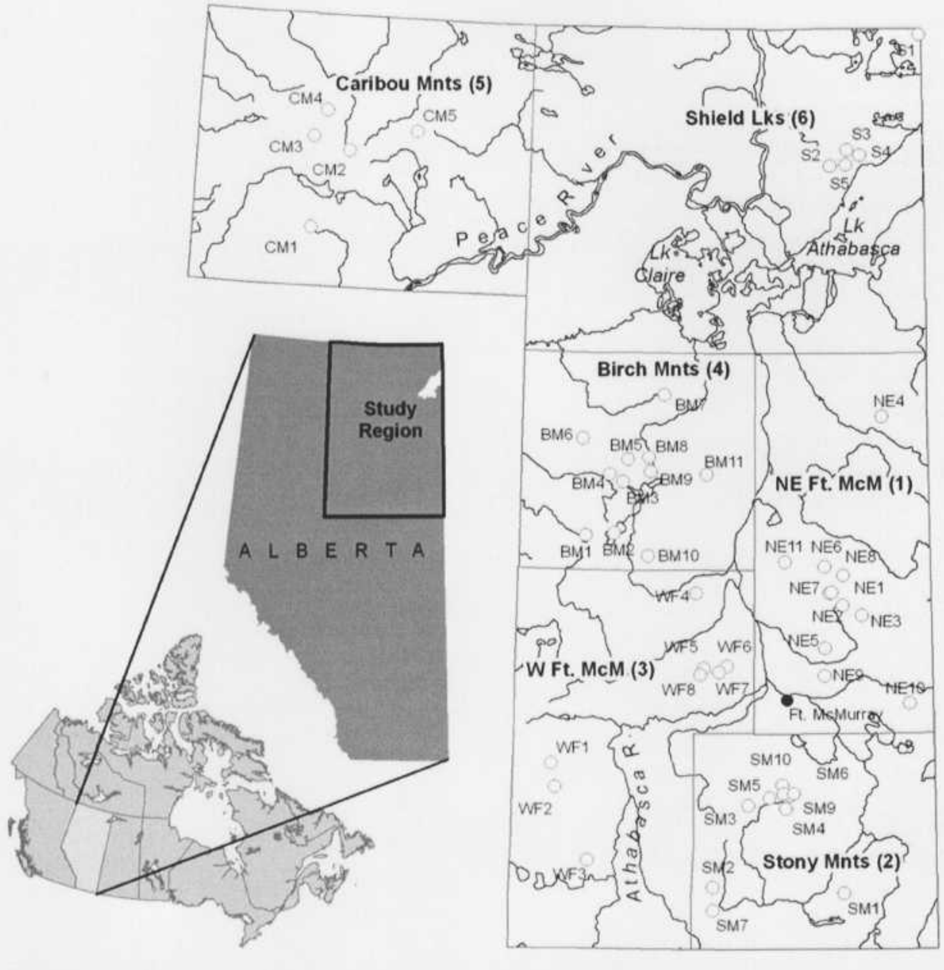


Figure 1.4 Map of study sites illustrating location of lakes within six sub-regional areas. Sites are labelled according to their sub-regional ranking, 1–6. Major rivers and lakes are labelled, as is the town of Fort McMurray. Inset shows the location of the study region within Canada and the province of Alberta.

IV. Methods

Methods outlined in this section detail the development of the various components used in the stable isotope mass-balance model, from first-hand field-based sampling to compilation of baseline climatic and isotopic data sets, where appropriate. Required model input parameters and variables are also discussed. To set the stage, Table 1.3 outlines all isotope mass-balance model input factors, their source, the type of data and units as expressed in the model, the date of production (when relevant), and the manipulation and/or calculation required to generate the information.

Annual Field Data Collection

Field collection of isotopic samples took place during 2002, 2003 and 2004 in the late summer/early fall period. Samples were collected from the pontoon of a single-engine fixed-wing Beaver, and helicopters were used to access small water features and detailed monitoring sites. For lakes greater than 2m in depth, a composite water sample was collected at the deepest part of the lake by multiple hauls of an integrated polyvinyl chloride tube to euphotic depth (2 times the secchi disk depth) or 1m above the lake bottom. For lakes less than 2m deep, a composite sample was created from 5–10 collections at 0.5m at different locations around the lake in order to repress spatial heterogeneity, if present. Water was transferred from the composite sampler to a 30mL airtight high density polyethylene container and sent to the University of Waterloo for standard analysis of stable isotopes $\delta^{18}O$ and $\delta^{2}H$ by mass spectrometry within two weeks of field data collection. Within the water cycle, isotopic abundances of both $^{18}O/^{16}O$ and $^{1}H/^{2}H$ are small; therefore, observations are most commonly expressed as delta values in per mil relative to Vienna Standard Mean Ocean Water (VSMOW) as a ratio value (see Coplen 1996), such that $\delta_{sample} = 1000((R_{sample}/R_{VSMOW})-1)$, where R represents either $^{18}O/^{16}O$ or $^{2}H/^{1}H$. Values are also normalized to standard light artic precipitation (SLAP), with a $\delta^{18}O$ value of –55.5‰ and a $\delta^{2}H$ value of –428‰ (see Coplen 1995).

Table 1.3 Summary of isotope mass-balance model input factors, with details on source (with reference where applicable), type of data and units, date of data source, and information on data manipulation. GIS = Geographic information system, ASRD = Alberta Sustainable Resource Development, GPS = Global Position System, DBA = drainage basin area.

Data	*Source*	*Type/Unit*	*Date*	*Manipulation*
Physical				
Latitude	GIS	Point	2004	Created from lake centroid of lake polygons in GIS.
Longitude	GIS	Point	2004	Created from lake centroid of lake polygons in GIS.
Lake Surface Area	GIS	Polygon, km^2	1998-2000	Created from 1:50K air photography provided by ASRD.
DBA	GIS	Polygon, km^2	1998-2000	Created from contours, air photography (1:50K), DEMs (NTS, 1:50K), geology and peatlands.
Lake Volume	Field/GIS	mm	1998-2000	Calculated from field measurements, GPS data, and GIS lake surface areas.
Climate				
Precipitation (Precip2, Table 1.4)	CRU 0.5° New et al. 1999	Gridded, mm	Climatology: 1961-1990	Downscaled and interpolated from gridded climate data.
Evaporation (Evapo3, Table 1.4)	Hamon (NCEP) Kalnay et al. 1996 Hamon 1961	Gridded/ calculated, mm	Climatology: 1961-1990	Downscaled and interpolated from gridded climate data.
Temperature (Base Case, Table 1.4)	CRU 10" New et al. 2002	Gridded, C°	Climatology: 1961-1990	Downscaled and interpolated from gridded climate data. Flux weighted according to Gibson 2002a.
Relative Humidity (Base Case, Table 1.4)	CRU 10" New et al. 2002	Gridded, %	Climatology: 1961-1990	Downscaled and interpolated from gridded climate data. Flux weighted according to Gibson 2002a.
Isotope Model				
Isotopes; Lake	Field collected	‰ VSMOW	2002-2004	None
Isotopes; Precip	Bowen and Revenaugh 2003	‰ VSMOW	Up until 2002	None
$CK^{18}O$ / $CK^{2}H$	Gonfiantini 1986	Factors		Uses factors 14.2, 12.5
$\epsilon *^{18}O$ / $\epsilon *^{2}H$	Horita and Wesolowski 1994	Modelled		Uses temperature (flux-weighted)
$\epsilon k^{18}O$ $\epsilon k^{2}H$	Gonfiantini 1986	Modelled		Uses CK & relative humidity
$m^{18}O$ / $m^{2}H$	Allison and Leaney 1982	Modelled		Uses ϵ *, ϵk & relative humidity
$\delta A^{18}O$ / $\delta A^{2}H$	Gibson et al. 2002	Modelled		Based on latitude, ϵ * & fraction of ϵ
$\delta *^{18}O$ / $\delta *^{2}H$	Gibson et al. 2002	Modelled		Uses relative humidity, δA, *, ϵk

The annual sampling schedule was established by Alberta Environment's Acid Sensitive Lakes program in 1999. The lakes were typically sampled once a year, a routine based on the relatively narrow seasonal variability of chemical characteristics in large lakes located outside the Wood Buffalo region (McEachern, unpublished material). In 2004, the seasonal program was implemented to capture the variability of lake water isotope signatures and chemistry present on a month-to-month basis through the open water season and to ascertain that fall sampling at small and shallow lake sites is representative of the average yearly isotopic flux.

Seasonal Field Data Collection

Ten lakes were chosen for seasonal sampling with the intent of collecting more detailed information to be used in the investigation of uncertainties in the water balance calculation and for validation of the isotope mass-balance model on a seasonal basis. This phase of the seasonal sampling involved collecting data from hydrologic nodes within the lake systems, including inflows, outflows, open water and wetland zones within the ten seasonal study catchments over a four-month period during summer 2004. Capturing this information allowed for a more accurate definition of watershed hydrology. Seasonal lake fluxes were investigated on a month-to-month basis to determine how variable the system was during the open water season and to ascertain that annual sampling periods were capturing the most evaporative condition. Open water or perennial wetland systems may contribute flow to the study lake and represent evaporative surfaces within the catchment. It was important to measure the amount of throughflow or evaporation from open water systems to understand how these surfaces may be affecting or interacting with the lake and catchment hydrology. Studying hydrological outflows from a lake body also helped to explain the system by determining that no out-of-basin sources of water (such as deep groundwater) were bypassing the lake to significantly contribute to outflow waters.

Seasonal sampling also involved installing precipitation collectors in each of the ten study catchments. Installing new precipitation collectors and sampling existing precipitation gauges in the Fort McMurray network assisted the field program by verifying the isotopic composition of precipitation. Isotopic signatures in precipitation used in the model were based on values obtained from a web-based tool (Bowen and

Revenaugh 2003, Bowen and Wilkinson 2002). The tool generates isotopic estimates for precipitation based on data from GNIP (www.isohis.iaea.org). The seasonal variation of isotopes in precipitation collected at ten lakes aided in validating the isotopic signatures obtained from the Bowen and Revenaugh (2003) source.

The gauges were designed to capture precipitation for isotope sampling rather than to measure volumetric amounts of precipitation. The gauges were constructed from an 8" diameter funnel, connected to a high-density polyethylene (HDPE) 4-litre jug with polyethylene tubing and sealed with silicon. They were fixed onto tree stumps at the edges of lakes with clamps and duct tape, and filled with 1" of mineral oil to preclude evaporation from the collected precipitation. In late summer 2004, the collectors were replaced with new versions of a similar design that did not require mineral oil, so that the water collected could also be used for chemical analysis.

Deep groundwater wells can be found throughout the study area, and, in theory, sampling of these wells would have allowed for mapping of deep groundwater isotopic composition. This would have enabled understanding of regional groundwater isotope signatures and identification of wetlands and lake systems that are connected to regional groundwater sources through partitioning of deep and shallow groundwater signals in lake water. Many of the wells are found on leases (either active, inactive or in the beginning phases of operations) in the area, which made it difficult to obtain access to them. At a selected number of sites, sampling was arranged through the leasers and their contracted water technicians; unfortunately, the eventual result of this effort was only one water sample (Conoco Phillips). However, a study conducted in 2002 by the Alberta Geological Survey provided isotopic data from 40 wells in the southern part of the study area. The information obtained from this study was considered sufficient to typify regional groundwater signals from the survey area. A spatial analysis of isotopic variations in deep groundwater, however, would be very useful and future studies may want to consider undertaking this sampling.

Detailed studies at five lakes were the backbone of the seasonal monitoring program. At each of these study lakes, shallow groundwater piezometers were installed to collect incoming isotope signatures. Piezometers were installed at one or two locations around each lake to extract shallow groundwater samples. A minimum of three piezometers were installed in each location in vertical transects upslope of the lakes. Transects were installed at two separate locations around the lake at sites BM7, SM9, NE7, and NE11 (Kearl Lake). Lake SM7 has one single transect of 6 piezometers. The mini-piezometers were designed, according to specifications contained in Lee and Cherry (1978), as follows. A series of 3/16" holes were drilled into the lower 10 cm of a 2 m long HDPE 0.5" diameter tube. A 200-micron diameter Nitex mesh sock was sewn around this section of the tubing and fixed to the tube with duct tape to filter sediments from the water sample. A hollow metal pipe with a drive head was driven down 1.2–1.5 m into the ground with a sledgehammer, and the 0.5" plastic tube was inserted into this metal casing. After the casing was removed, a small flexible plastic tube was inserted into the larger plastic tube. A hand pump was attached to the flexible tubing to extract the shallow ground water.

After installation the piezometers were pumped and sampled each month during the seasonal sampling period to extract 30ml of water for isotopic analysis. Where hydraulic conductivity provided suitable recharge rates, wells were purged prior to extracting a fresh sample. Soil samples were collected at the five study lakes in the areas where mini-piezometer transects were installed. Soil was extracted using a coring tool and qualitatively observed in the field for properties such as soil type, texture and moisture content. Soil samples were not taken from each of the representative cover types found throughout the watershed. Soil sampling for properties such as hydraulic conductivity and isotopic enrichment allows for more in depth understanding of the amount of water held in a particular soil unit and the water movement within a watershed. Sample collection from the soil would therefore assist to more clearly define hydrologic pathways. Sampling of soils from detailed study catchments is recommended for future studies.

Physical Parameters

Physical data was required to provide isotopically-based estimates of residence time and water-yield (see Eq. [10] and [11]). Watershed and lake physical parameters were estimated in a Geographic Information System (GIS) using 1:50,000 orthophotographs, the existing National Topographic System (NTS, 1:50,000) database, and NTS digital elevation models (DEMs, 1:50,000) to digitize lake surface area, and lake and catchment elevations. Although air photography was collected over the period of 1998-2000, the lakes basin outline and land surface was not expected to increase or decrease to a large extent in the two to four years from the creation of this data set. DEMs were employed to delineate the initial watershed outline (drainage basin areas, DBA), then bog and fen features and surficial geology were used to adjust the boundaries appropriately, allowing for incorporation of potential sub-surface flow patterns not reflective of surface topography (Devito *et al.* 2005a, Vitt *et al.* 1996). The effective DBA (eDBA) is calculated as outlined in Gibson et al. (2002).

Lake centroids based on surface areas were used to generate specific latitude and longitude positions for further extraction of variables such as precipitation. Slope was derived using 1:20,000 DEM tiles, and was then mosaiced and analysed using Environmental Systems Research Institute's (ESRI) Spatial Analyst functions (ESRI 2000). Lake bathymetry was measured at three to five multiple transects across lake sites, using a sounder to record depth at equal time intervals while traveling at a constant speed and bearing between initial and terminal positions, which were recorded using a Garmin hand-held global position system (GPS). These point data were transferred into the GIS and interpolated to create depth polygons of varying intervals.

Lake volume was calculated, based on the surface area of slices at discrete depth intervals, using a frustral equation (McEachern, pc). This method was compared to other approaches for calculating volume, which included using ESRI's 3D Analyst function to create triangular irregular network (TIN) for volume calculations (ESRI 1998), ESRI's Spatial Analyst to create a grid to derive volume (ESRI 2000), maximum depth multiplied by area, mean depth multiplied by area and two other means of calculating volume (Bahr *et al.* 1997, Driedger and Kennard 1985).

Alberta Sustainable Resources Development, in conjunction with timber production companies (e.g., Alpac) and the oil sands operators, have developed detailed land cover data for the region. This data set was obtained for use on this project, and was examined in a GIS. However, the data set did not include information such as wetland type, including bog, fen (rich and poor types), marsh, swamp and shallow water. As well, the data set required field verification using on-the-ground or air-based observations. Photographs, field sketches and comparative mapping (using existing data sources plotted onto field maps) were undertaken to distinguish wetland types and to verify existing land cover mapping data. Ground-truthing also served to verify locations of channels and drainage features, and to examine catchment boundary mapping in the cases where existing data were not sufficient to determine basin edge.

Climate Variables

Temperature, precipitation, evaporation and relative humidity data were downloaded and extracted for the study lakes from several different climatological databases (Table 1.4). The monthly mean values for each climate variable were summarized by lake site into either a total (for evaporation and precipitation) or an open-water seasonal average (for temperature and relative humidity). Temperature and relative humidity were in turn flux-weighted by evaporation; this procedure will be discussed later in the chapter. After analysis and consideration of the range of available data for climate variables, four final data sets (demarcated with an asterisk in the Table 1.4) were selected for the final isotopic mass-balance model. Each of the climate data sets required specific manipulation procedures for extraction and processing to a GIS for interpolation at each lake site. The filtering of climate data is explained in detail below. Filtering results from climate data analysis are presented in Figs. 1.11 – 1.14, while extraction and manipulation procedures are outlined in Appendix A.

All climate data were reviewed in detail to decide which was the most applicable for use in the isotope mass-balance analysis (Bonsal *et al.* 2003). Average yearly results were graphed together and the differences were examined between specific models in a bivariate pulse diagram. The standard deviations of all data sets were calculated for each lake site, and an attempt was made to eliminate data sets based on their status inside and outside of a standard deviation curve. However, the technique proved to be less selective than anticipated, and therefore each data set was dealt with individually to determine which was the most appropriate for use in the final data isotope mass-balance model, as described below.

Evaporation data ranges were examined and the data that best represented the precipitation minus evaporation (P–E) relationship for this region were selected for use (denHartog and Ferguson 1978, Winter 1989). The method selected for use in the final version of the isotope mass-balance model was a Hamon-approach using the NCEP temperature data set (Hamon 1961, Kalnay *et al.* 1996). Other estimates for evaporation

(Abraham 1999, Morton 1983) suggested open-water lake evaporation in the Fort McMurray region was 572 mm based on data from 1912–1996. This estimate was considerably higher than any other value examined, but was the only other source for local evaporation estimates based on long-term observation data, as evaporation data are not collected at the Fort McMurray climate station.

The remaining data sets were selected based on their relationship to other data sets. The CRU 0.5-degree precipitation data set was selected for the final version of the isotope mass-balance model for the P-E relationship as expressed above, and because the lake sites near Fort McMurray fell close to the values observed by the Fort McMurray climate station. The data closest to the approximation given by the Fort McMurray climate station (3062693; WMO ID 71932, MSC 2004) were also used in the final data isotope mass-balance model for temperature and relative humidity data sets.

To determine relationships between the three individual years of study, and the pre-study year, these data were examined and compared to the climatology estimates at the Fort McMurray climate station. Temperature and precipitation data was available for the Fort McMurray climate station for the 1971- 2000 climatology and for 2001 (pre-study year), 2002, 2003, and 2004. Min, mean and max temperature data was examined by yearly average, May to October average, and each individual monthly period. Snow, rain and precipitation data was available and analysed by totals from each year and May to October periods. Monthly values for snow, rain and precipitation were also examined but in a separate analysis as the monthly values were not compatible with yearly totals. All data was found to approximate a normal distribution but was highly correlated. Therefore, a paired Student's T-test was applied to analyse the difference in means between the climatology and individual yearly assessments. A discussion of these results is included in both the climate analysis results and in the section outlining the regional scale implications of study results on boreal plains hydrology. Table 1.5 lists all data and analysis results are included in Table 1.6.

Table 1.4 List of climate variables and data sets employed for extraction. References are listed.

Climate Variable	*Gridded Data*	*Global Climate Model Data*	*Other*
Precipitation	CRU 10" (New *et al.* 2002) *CRU 0.5° (New *et al.* 1999) ANUSPLIN (Hutchinson 2000,Price *et al.* 2000) CANGRID (Louie *et al.* 2002) IDW (McKenney *et al.* 2001. PRISM (Daly *et al.* 1994)		
Evaporation	NCEP/NCAR (Kalnay *et al.* 1996, *www.cdc.noaa.gov/*) ECMWF (Uppala 2001, www.ecmwf.int/)	CGCM2 (Flato *et al.* 2000, Kim *et al.* 2002)	Hamon -CRU 0.5° (New *et al.* 1999) Hamon -CRU 10" (New *et al.* 2002) *Hamon -NCEP (Kalnay *et al.* 1996) Thornthwaite PET (Thornthwaite 1948) Thornthwaite AET (Thornthwaite 1948) Hydrologic Atlas (denHartog and Ferguson 1978) Morton (Abraham 1999, Bothe and Abraham 1987, 1993)
Temperature	*CRU 10" (New *et al.* 2002) CRU 0.5° (New *et al.* 1999) NCEP/NCAR (Kalnay *et al.* 1996) ANUSPLIN (Hutchinson 2000, Price *et al.* 2000) CANGRID (Louie *et al.* 2002) IDW (McKenney *et al.* 2001.) PRISM (Daly *et al.* 1994)		Fort McMurray (MSC 2004)
Relative Humidity	*CRU 10" (New *et al.* 2002) NCEP/NCAR Surface (Kalnay *et al.* 1996, *www.cdc.noaa.gov/*) NCEP/NCAR 1000mb (Kalnay *et al.* 1996 *www.cdc.noaa.gov/*) ECMWF (Uppala 2001 www.ecmwf.int/)	HADCM3 (Pope *et al.* 2000)	

The use of gridded reanalysis data to calculate climate parameters for use in this water-balance model was considered in depth, as the application of these data has yielded poor results in hydrologic model scenarios by some workers (see Whilby *et al.* 2000). The limitation of these data include: the coarse level of information provided, the spatial mismatch between scales of data and scale of application (Lettenmaier *et al.* 1999), the issue of interpolation across space that may not be reflective of conditions between point measured stations (Bennett *et al.* 1984), and the variation inherent in the landscape that is often not represented by the station (Pietroniro *et al.* 1996). For example, a lake system or the presence of open-water bodies or wetlands within a catchment can alter climate parameters, such as relative humidity or evaporation (Brutsaert 1982). However, given the complete lack of long-term, reliable point-based estimates for the headwater study catchments, these gridded data were the best available and provided a first approximation of climate parameters across the regional lake systems. Additionally, considerable attention was placed on evaluating and comparing the climate data, thus proving a clear choice for the best data set available to represent climate in this area (Abraham 1999, Bothe and Abraham 1987, 1993, Daly *et al.* 1994, Flato *et al.* 2000, Hutchinson 2000, Kalnay *et al.* 1996, Kim *et al.* 2002, McKenney *et al.* 2001., New *et al.* 1999, New *et al.* 2002, Pope *et al.* 2000, Price *et al.* 2000, Uppala 2001). More detailed in-catchment study was not possible given the project limitations; collecting climate data at each of the 50 lakes would have been very costly to instrument and monitor.

Moreover, an isotopic mass-balance approach that did collect climate information based solely on year-to-year measurements would have only provided information for the three years of analysis. These three years might have been exceptional and this would have provided a skewed view of the long-term water balance occurring within these systems. The aim of the project was to provide a long-term estimate of water balance at these systems that could be relied on year-to-year despite shifts or alterations in the hydrologic cycle that may occur on a seasonal or annual basis. To collect information and obtain an annual average climate signal representative of conditions across the region would require 10 years of analysis or longer, a time frame that was simply too long given the requirements of the project. Although, there was a concern of the reliability of the gridded climate data as applied, rigorous model testing of input factors (outlined in the following sections) proved that relative humidity was the only sensitive climate variable. Thus, a recommendation of this research would be to focus on developing a benchmark estimate at one or two lake sites for relative humidity to provide adequate measures of accuracy, and a tool to adjust or correct relative humidity estimates.

Isotopic Data

Isotopic data were collected and put into the data model from two separate data sources: lake water and precipitation isotopic signals. The isotopes in lake water were collected in the field and analysed as described earlier in this section. Analytical uncertainties for $\delta^{18}O$ are ±0.1‰ and ±2‰ for $\delta^{2}H$.

The isotopic signal in precipitation is based on reworked GNIP data published by Bowen and Revenaugh (2003, www.waterisotopes.org). These data are available as yearly averages or as monthly summaries. The data were examined to ensure they were comparable; monthly and yearly values were compared to determine similarities and differences. The monthly data were flux-weighted (see next section) and input into the isotope mass-balance model to determine if the flux weighting could replace the fitting techniques described in Gibson (2002a). Both iterations (yearly and monthly flux weighted by evaporation and by amount) were tested in the isotope mass-balance model for comparison of results. The final data isotope mass-balance model uses the yearly data values.

Evaporation Flux Weighting

The evaporation flux weighting approach (Gibson 2002a) was applied to the climate variables of temperature, relative humidity and the isotopes in precipitation. Evaporation flux-weighting was undertaken for each lake site by multiplying factors by the monthly evaporation average and then summing those values and dividing by the annual sum of evaporation. This method of weighting climate and isotope data was used in order to emphasize the processes occurring during the open-water evaporation season. For example, low temperatures occurring during January at lake sites do not affect the open-water hydrologic processes because lakes are frozen over during this period. Additionally, evaporation occurring during the month of August could influence temperatures and relative humidity relationships that would not otherwise be emphasized using alternate methods of weighting. The 50-lake network was used as a test case to determine how the concept would work on a real data set using monthly values of evaporation to weight each parameter (as only theoretical concepts are presented in Gibson 2002a). Evaporation flux weighting involved multiplying the specific monthly climate variable by the monthly evaporation and then dividing by the annual total evaporation to get a weighted average flux for each lake site. This revised estimate for climate variables was input into the isotopic data model for use in calculating new variables and to generate the final output results. The flux-weighted values for isotopes in precipitation were not applied; results are discussed in more detail in the following section.

V. Results and Discussion

Defining $\delta^{18}O$ and $\delta^{2}H$ of model inputs

Lake water: The isotopic composition of lake water was found to range from –16‰ to –7.5‰ for δ^{18}O and from –140‰ to –85‰ for δ^{2}H, this range is attributed mainly to differences in hydrological flushing of the individual reservoirs, as atmospheric conditions were not significantly different among the study sites. Relatively stable interannual values, and adherence to a single EL (Fig. 1.5), suggest systematic evaporation with similar kinetic fractionations and relatively invariant isotopic composition of atmospheric moisture across the region. The regression equation for the 2002 data set is $y = 5.0627x - 52.192$, $r^2 = 0.98$; for 2003 it is $y = 5.3577x - 48.066$, $r^2 = 0.96$; and 2004 is $y = 5.454x - 48.86$, $r^2 = 0.96$. The average for these three years equals $y = 5.2964x - 49.659$, $r^2 = 0.98$, given as the local evaporation line. Average values for each lake for the three-year period were used as input to the isotope mass-balance model. Average interannual differences (1 std) ranged from 0.1‰ to 1.4‰ for δ^{18}O and from 0.7‰ to 7.3‰ for δ^{2}H, and standard deviations for 2002, 2003 and 2004 are 2.95, 2.71 and 2.95‰ for δ^{18}O and 12.35, 15.13 and 14.87‰ for δ^{2}H, respectively. This information becomes a useful overall measure of deviation from steady state and also can be used as a tool for sensitivity analysis (Knoller and Strauch 2002), as discussed later.

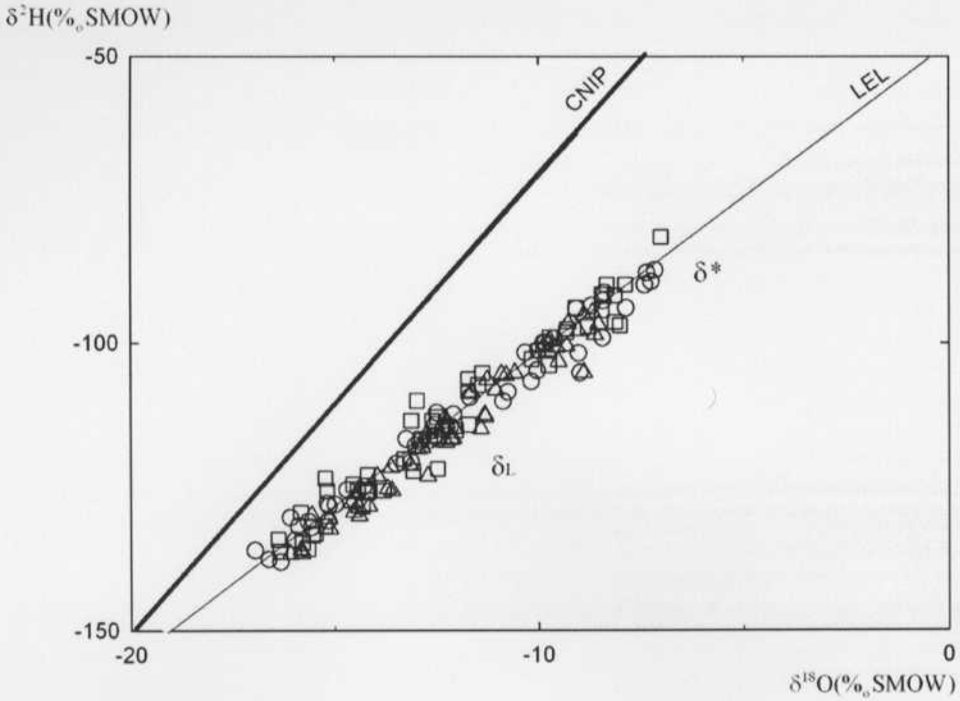


Figure 1.5 Results of three annual sampling programs, 2002–2004. Circles, squares and triangles depict the averages lake water values for the 2002, 2003, and 2004 study sampling years, respectively (n = 49).

Seasonal cycles of $\delta^{18}O$ and $\delta^{2}H$ variations in lake water were measured more regularly at a subset of ten lake sites during June to September 2004, to compare non-steady state effects and to ascertain potential bias due to timing of the individual water surveys (Fig. 1.6). Summer monthly isotopic compositions were collected to ensure that variation across the open-water season was limited and was synchronous with previously collected yearly samples. This test was also completed to determine the timing of waxing and waning isotopic composition. Typically, June samples were the most depleted, whereas August samples were the most enriched, reflecting shifts toward higher evaporation and reduced snowmelt input toward the late summer. Seasonal sampling suggested that typical variations in isotope composition were systematic, and varied by ±1.0‰ in $\delta^{18}O$ and ±4.5‰ in $\delta^{2}H$ across the four months of the summer season at ten select lake sites. While this analysis helps to establish uncertainty in the long-term averages, it also leaves an overriding impression of a relatively steady-state system with a very high signal to noise ratio, wherein isotopic shifts related to known seasonal variability in lake water budgets do not effectively mask the lake-to-lake variations (±2.6‰ in $\delta^{18}O$ and ±12.9‰ in δ^2H). This is unlike lake systems studied in the continental Arctic (Gibson 2002) where non-steady state conditions predominate due to stronger seasonality and snowmelt-driven flushing.

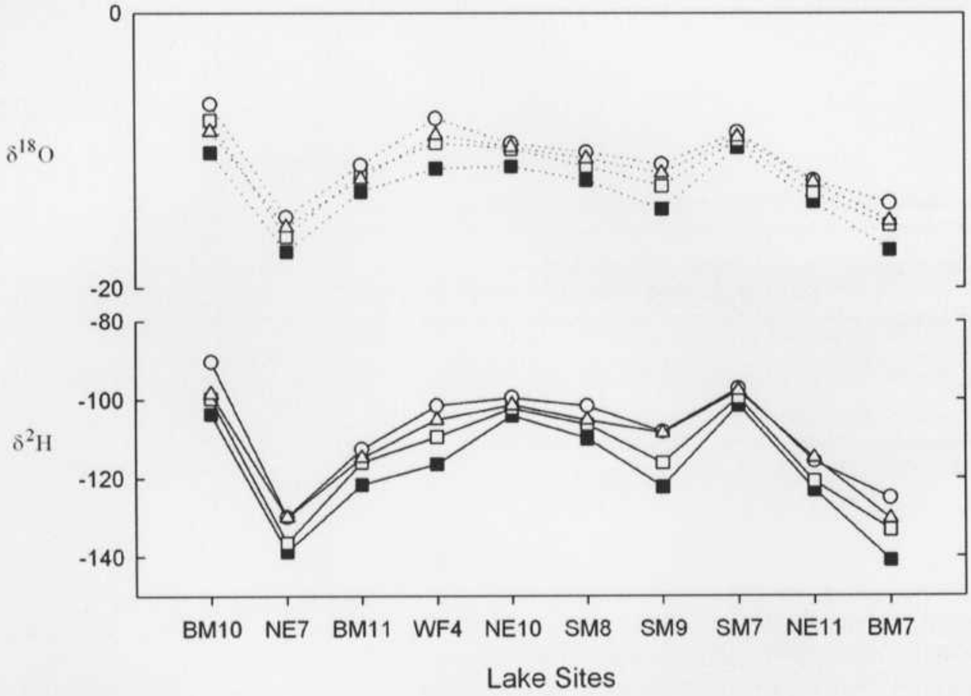


Figure 1.6 Monthly variations at lake sites for $\delta^{18}O$ and δ^2H. Samples were collected under the seasonal sampling program. Samples are distinguished by month, where June, July, August and September samples are shown as black squares, open squares, open circles and open triangles, respectively.

Precipitation: In $\delta^{18}O$ - δ^2H space (Fig. 1.7) the isotopic signatures of precipitation collected in each of the ten seasonally sampled lake systems is compared with the monthly climatology of Bowen and Revenaugh (2003). This data set was considered to be the best available estimate of modelled isotopes in precipitation for this region, as it relies on station data (GNIP) but also accounts for flux in isotopic compositions based on latitude, elevation, and other factors; and as explained below, proved to be an accurate estimate when tested against field sampled observations. The seasonal spread between field-sampled precipitation data are greater than the range provided by the model-derived data points, but in general the model and observed data sets show good agreement. On average, precipitation, unlike lake water isotope signatures, varies less from lake-to-lake and more greatly on a month-to-month basis at the ten lake sites (±2.2‰ compared to 1.0‰ in $\delta^{18}O$ and ±11.6‰ compared to ±6.6‰ in $\delta^{2}H$ for summer months and lake sites, respectively). Maximum enrichment in precipitation does not occur during August, as it does in the lake isotopic water samples, marking the difference between primary isotopic composition and waters that have undergone systematic enrichment due to evaporative fractionation effects.

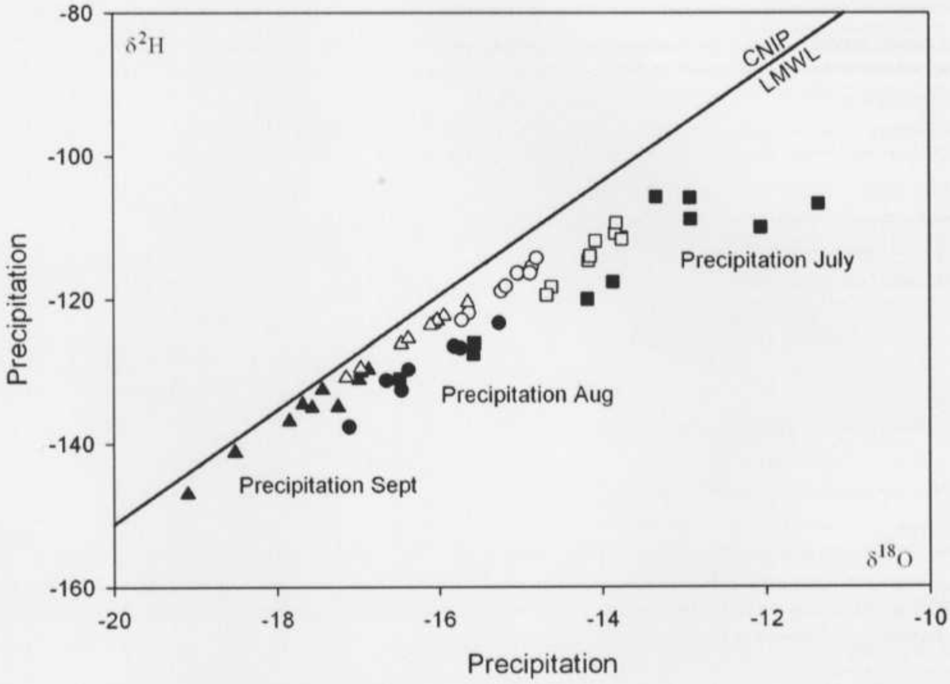


Figure 1.7 Comparison of field-sampled (solid symbols) and interpolated values of $\delta^{18}O$ and $\delta^{2}H$ in precipitation for the ten intensive study sites. Interpolated values are based on the model of Bowen and Revenaugh (2003) (open symbols). Note: Squares = July, Circles = August and Triangles = September.

Groundwater: Groundwater data presented in Fig. 1.8 are a composite of field-sampling surveys from this study and previous results reported by Alberta Geological Survey (AGS) from a regional borehole network (Lemay 2002). The 44 AGS samples were collected from various groundwater formations, namely, Quaternary drift, Quaternary-Tertiary buried channel aquifers and underlying bedrock (i.e., Lower Cretaceous: Viking, Colony, Grand Rapids and Clearwater; and Lower Cretaceous:

Wabiskaw Member and McMurray). Results from the Quaternary and Quaternary-Tertiary buried channel aquifers, underlying bedrock and shallow groundwater sampled in the intensive study watershed are shown in relation to the CNIP-based MWL and LEL from the ten intensive study watersheds. As shown (Fig. 1.8), the Quaternary samples and the field-collected samples plot in close proximity to the LEL line, while the Cretaceous groundwater samples align more closely with the MWL. Based on review of stratigraphic maps of the various units in the Athabasca Oil Sands area (Mossop and Shetsen 1994), the Quaternary formations are located much closer to the surface than the Cretaceous samples. The Quaternary buried aquifer channels may come in contact with surface water occasionally via river channelling and/or where glacial scour has eroded away the top layers at lake sites (Lemay 2002). Therefore, the water at these sites is potentially closer to shallow groundwater and may align more closely with input precipitation signals.

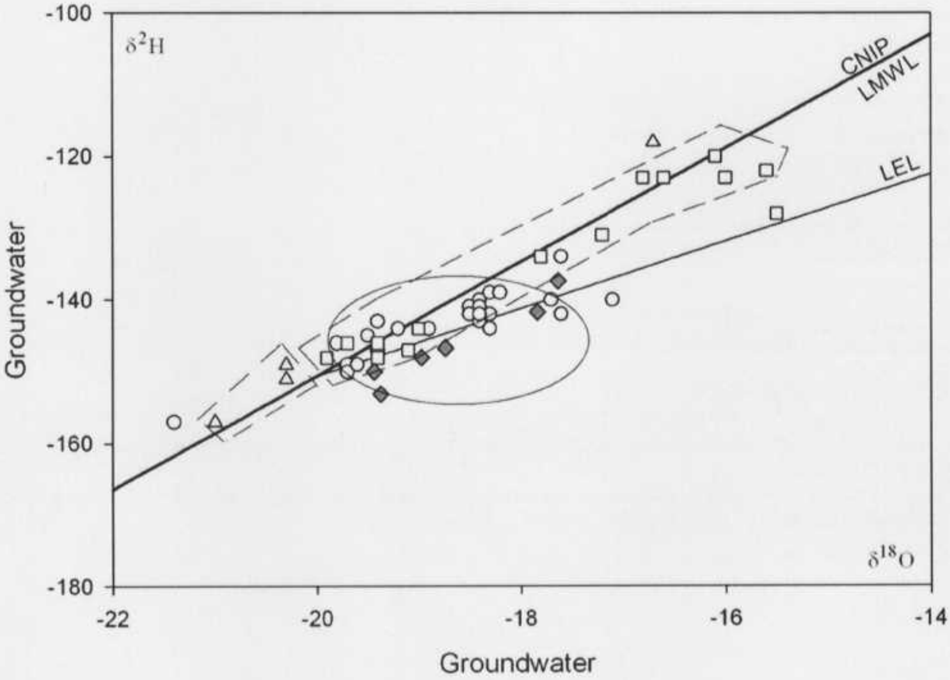


Figure 1.8 Groundwater isotopic signatures from the Fort McMurray area shown in relation to the Canadian CNIP LMWL and the LEL (this study). The oval circle encompasses data that lies along the LEL, shown by the open circles (Quaternary and Quaternary-Tertiary buried channel aquifers, source Lemay 2002), and the grey diamonds (shallow groundwater, collected at intensive sites in this study). The dashed line and the dashed-dotted line illustrates the groundwater sources that fall along the CNIP LWML, illustrated with open squares and triangles (Lower Cretaceous formations, see text for description of individual units).

To test this theory, the Quaternary drift samples were combined with the average field-collected shallow groundwater samples and the isotopes in precipitation collected during summer 2004 in ten detailed study lakes (Fig. 1.9). Two samples from the Lower Cretaceous (Viking, Colony, Grand Rapids and Clearwater), one Quaternary drift site and the Conoco-Phillips sites were also included, as they fell into alignment with the $\delta^{18}O$ - δ^2H regression line based on the previously listed sites. This new local meteoric water line (LMWL) has a slope of 6.9 as opposed to the CNIP MWL, which has a slope of 7.9. This new LMWL was used to update the isotope model (see Section entitled 'Testing isotope mass-balance model outputs') with new intercept data points representing isotopic signals for precipitation.

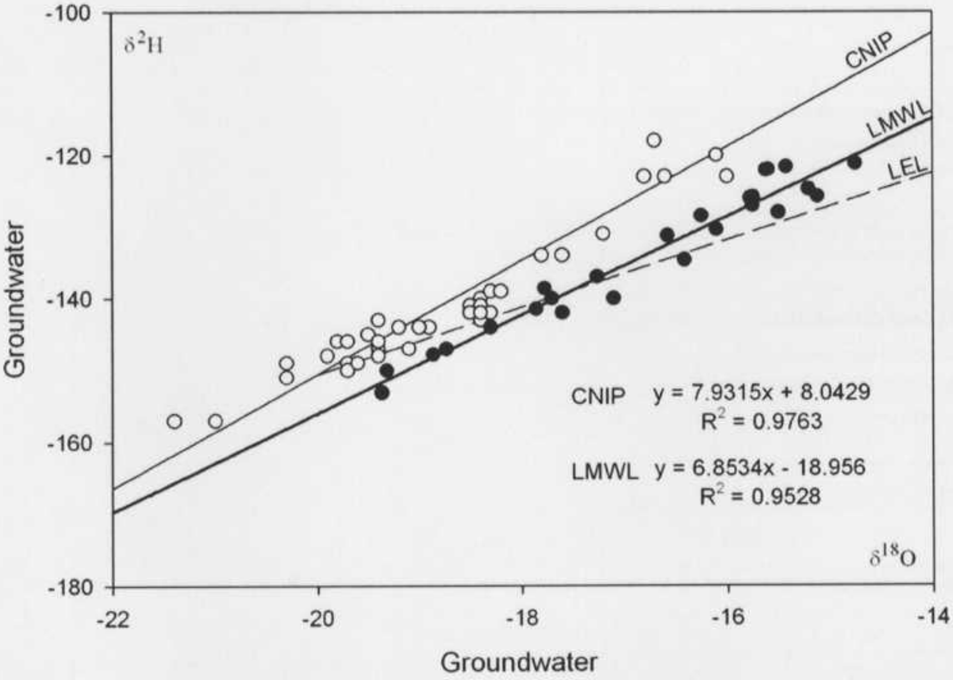


Figure 1.9 New LMWL line created from field-collected precipitation (this study), shallow groundwater and Quaternary drift samples (Lemay 2002). The black circles represent groundwater and locally collected precipitation water samples used to generate the new LMWL; open circles represent the remainder of the groundwater database (Lemay 2002).

River waters: Samples were collected from local rivers (shown with black circles in Fig. 1.10) in order to develop a local isotopic runoff signal. Most local rivers illustrate a runoff profile in $\delta^{18}O$ - $\delta^{2}H$ space falling between the end of the LEL and the intercept of the LEL and MWL; however, a few systems appear to contain evaporated waters and extend well into the LEL. These rivers include the Kearl Lake, Beaver Creek and Gregoire River. The Kearl Lake outlet August sample is much more enriched than the June sample (–15.11‰ vs. –13.58‰ $\delta^{18}O$, respectively). Beaver Creek, which appears to drain Mildred Lake, is also highly enriched, possibly owing to the mixing in this system with processed waters. Notably, Gregoire River is the most enriched riverine system sampled; this river drains down from the Stony Mountains east to join with the Georges River, which then flows north to meet the Christina River. River flows were low during the sampling period, despite the early sampling date (June), which may have contributed to ponding and evaporation of the sample, or it is possible that the river passes through wetlands or lowland areas where significant evaporation could be occurring.

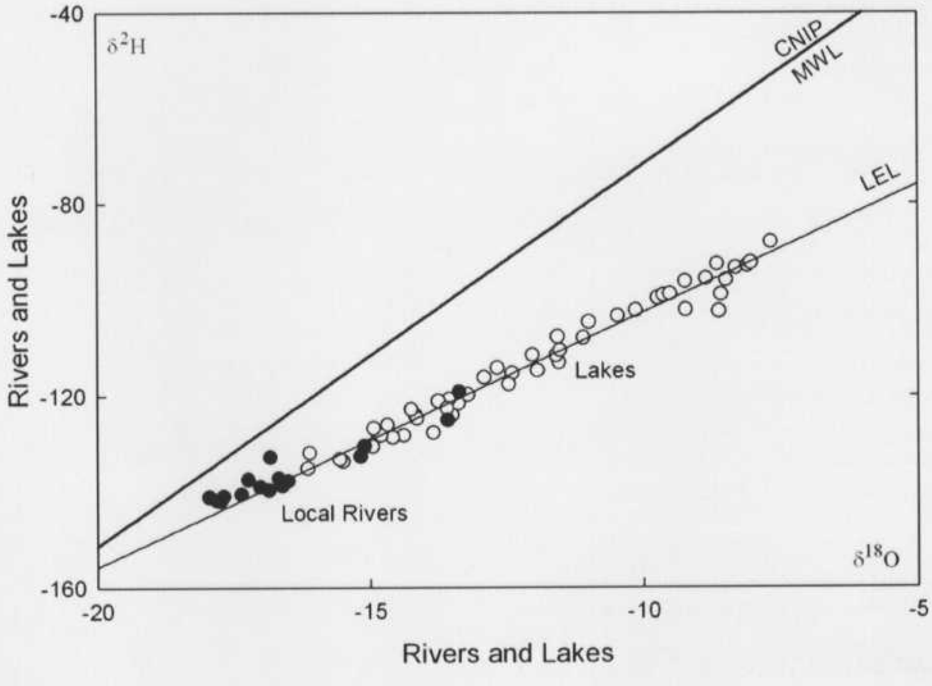


Figure 1.10 Isotopic signal from river systems located in the study area (dark points). Lake samples are shown with open circles and the light line illustrates the LEL. The CNIP MWL regression line is shown (dark line) as well.

In summary, this section of the thesis addresses all isotope mass-balance model uncertainties: including annual and monthly sampling of lake water isotopic signatures, monitoring of precipitation isotopic ranges and comparison to model input data (Bowen and Revenaugh 2003), and sampling of groundwater and river runoff signals. Isotopes in lake water were highly correlated ($r^2 = 0.98$) between the three study years (Fig. 1.5). In addition, monthly estimates of lake water isotopic signals (Fig. 1.6) show limited variation through the open-water season. Local samples of isotopes in precipitation also were close to the isotope mass-balance model input variables (Fig. 1.7), although the model-derived estimates have a narrower range of distribution and are less variable, perhaps reflecting the smoother nature of the interpolated GNIP precipitation station data (Bowen and Revenaugh 2003). Signal trends recorded through the months were observed at every lake site (with the exception of lake SM7) and are also reflective of signals logged at the Edmonton GNIP station (IAEA/WMO 2004). Groundwater collection from the seasonal lake systems is indicative of the intercept position of the LEL and the MWL (Fig. 1.8). Deep groundwater from (Cretaceous) formations may be a reflection of the long-term isotopic condition of the area, which is more closely related to the MWL (Lemay 2002). The use of the Quaternary formation groundwater isotopic data, in conjunction with field-collected precipitation and shallow groundwater samples, improved predictions of δ_P when the intercept formula (Dincer 1968) was used (Fig. 1.9). Runoff signals taken from local rivers (Fig. 1.10) also fall at a position near the intercept of the LEL and the MWL, indicating the local runoff signal is close to the signal for input precipitation and shallow groundwater sources. As earlier noted, one river system (Gregoire) could be experiencing evaporative enrichment along its course due to its meandering surficial drainage route.

Defining and testing climatic variables: Climate variables applied in the isotope mass-balance model were taken from the CRU 0.5° data set (precipitation), an NCEP-based Hamon estimate (evaporation) and the CRU 10" data set (temperature and relative humidity). The methods section of this thesis chapter details the reasoning for selection of each climate variable. Climate data were tested within the isotope mass-balance model framework, and for sensitivity to flux-weighting approaches; results of this testing are outlined in the following sections.

The results for the climate data analysis show the wide-range of variation across the climate data sets. The May to October average temperatures (Fig. 1.11) at lake sites range (on average) from 8.8° - to 10.8°C across lake sites. Standard deviations between each data set are a maximum of 1.5°. Temperatures decrease in all models at more northern locations. The CRU 10" data set is one of the highest records of temperatures for the lakes (on average) and was selected for use in the final version of the model, as shown below.

Yearly average total values for precipitation range from 413 mm/yr to 555 mm/yr at lake sites (Fig 1.12). Decreases in precipitation are shown between latitudes of ~55° - 58.5°N. However sites above latitude 58.5°N have more precipitation, owing to the occurrence of lake sites located at elevation within the Caribou Mountains and possibly microclimate effects occurring at sites above Lake Athabasca. The CRU 0.5° data set has the lowest values of precipitation within the data sets analysed. This data set was used in the final version of the isotope mass-balance model.

Evaporation data sets (Fig. 1.13) for the eight different options range between 389 mm/yr to 521 mm/yr at the 50 lakes sites. The average standard deviation between the data sets at specific lake sites is 54 mm. Some data sets provide estimates of higher levels of evaporation in the north, whereas other data sets illustrate lower evaporation occurring at northerly sites. The Hamon-NCEP estimate provides decreased levels of evaporation at northern lake locations. The Hamon-NCEP was used to estimate evaporation at lake sites in the final version of the isotope mass-balance model.

Relative humidity (Figure 1.14) does not vary greatly across the lake sites, the average standard deviation ranges from 0.5 – 1.6% for study lakes. This is illustrated by the relatively flat distribution of data points. A slight increase in relative humidity with latitude occurs in all data sets. Most data sets reported either unusually high or usually low data values, with the exception of the CRU 10" data set, and therefore were unsuitable for use in the isotope mass-balance model.

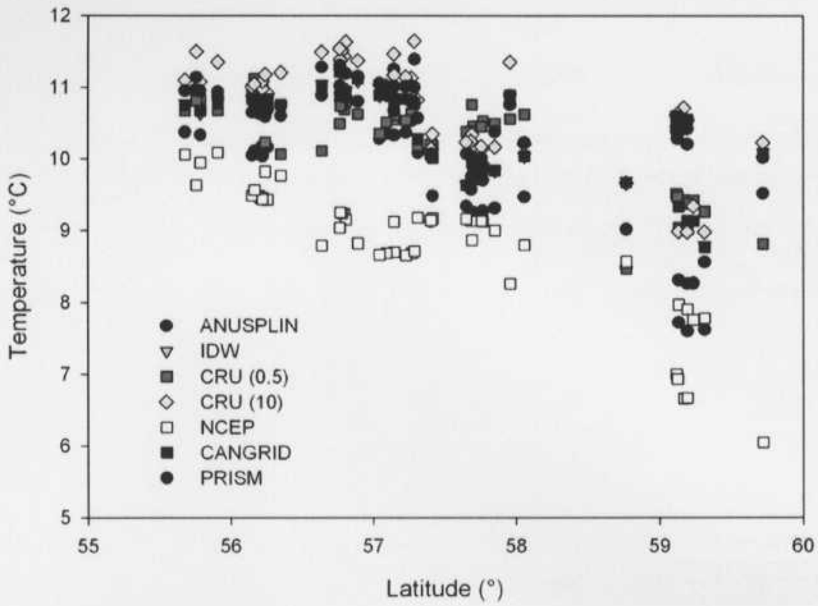


Figure 1.11 Temperature data (May to October average) in °C for the seven models analysed (see Table 1.4). Data is sorted by latitude. The CRU 10" data set, shown with a grey diamond, was used for the final version of the isotope data model.

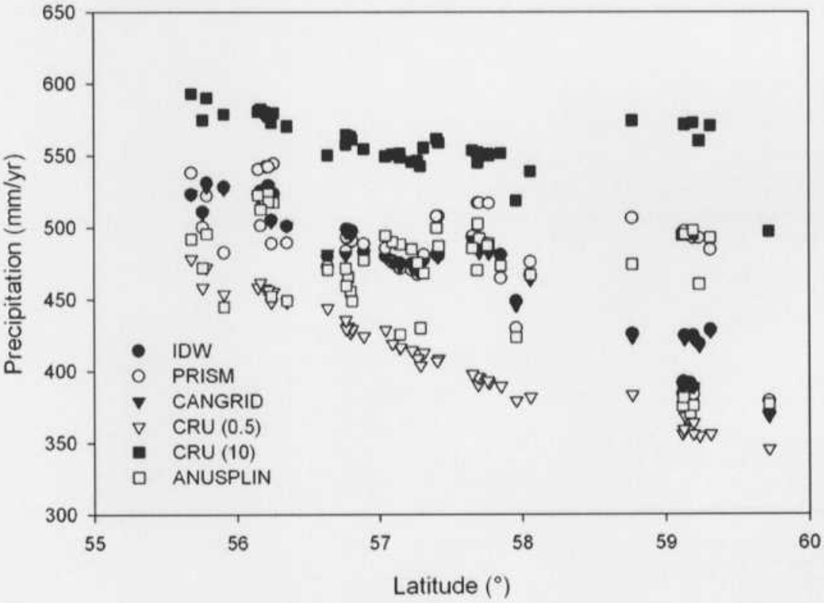


Figure 1.12 Precipitation (mm/yr) data for lake sites sorted by degrees of latitude. The open downward triangle depicts the CRU 0.5° data set, which was used in the final version of the isotope mass-balance model.

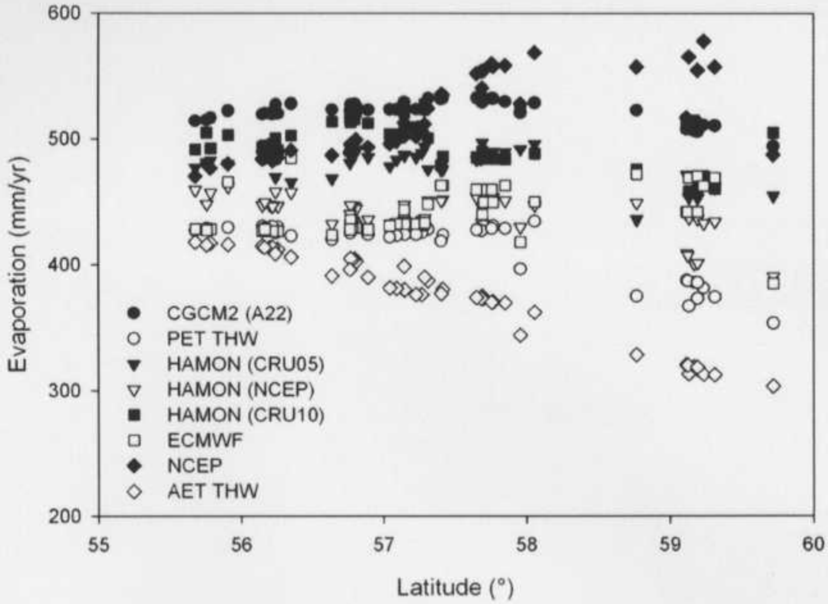


Figure 1.13 Evaporation (mm/yr) data for the lake sites sorted by degrees of latitude. Some data sets depict more evaporation at higher latitudes; others show lower evaporation closer to latitudes of 60°N. The Hamon-NCEP data set (open triangles) was selected for the final isotope mass-balance model.

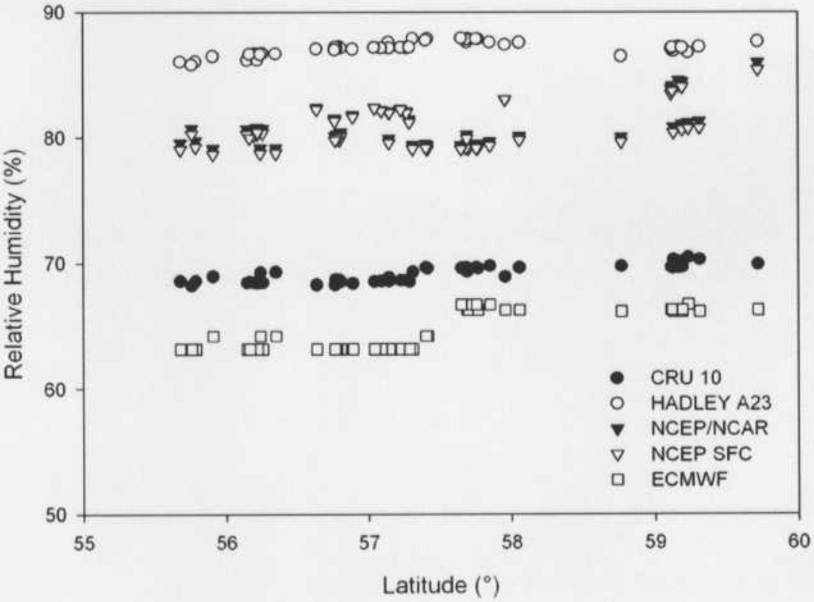


Figure 1.14 Relative humidity (%) for lake sites sorted by latitude (°). The CRU 10" data set was selected for use in the final version of isotope mass-balance model, as it is the most reasonable estimate of relative humidity for this region.

Variations in the climate across the three study years were measured using the Student's T-test statistic for normal variables (tested using the K-S statistic). Results are provided in Table 1.5 and Table 1.6. Differences between the long-term mean (1971 – 2000) for temperature (Table 1.5) and precipitation (Table 1.6) incurred on an annual, seasonal and monthly basis were examined for each of the three study years, and the pre-season year. Based on temperature differences alone, only 2004 differed from the long-term average climatology. Monthly rain or precipitation values were not different between any years, while monthly snowfall was significantly different in 2002. Yearly and seasonal differences for rain, snow and precipitation differed in 2001. These results indicate that only the year of 2003 was a 'normal' year in terms of the differences between the long-term climatology and the annual, seasonal and monthly variations in temperature and precipitation.

Table 1.5 Temperature data from the Fort McMurray Climate station. Results include long-term monthly climatology, and 2001 – 2004 monthly, and seasonal and yearly minimum, maximum and mean temperatures.

Year, Season or Month	*Climatology 1971 - 2000*	*2001 (pre-season)*	*2002*	*2003*	*2004*
Jan	-18.8	-8.4	-17.6	-16.6	-21.4
Feb	-13.7	-16.1	-10.6	-18.6	-10.6
Mar	-6.5	-5.6	-14.4	-10.6	-6.5
Apr	3.4	3.6	-2.9	3.9	3.0
May	10.4	10.4	6.7	9.3	5.7
Jun	14.7	14.3	15.6	14.0	13.3
Jul	16.8	17.6	16.8	17.6	18
Aug	15.3	16.7	14.3	16.1	12.7
Sep	9.4	11.6	9.0	9.5	7.9
Oct	2.8	1.0	-2.4	4.4	1.1
Nov	-8.5	-4.2	-7.3	-9.4	-5.8
Dec	-16.5	-15.4	-10.6	-12.1	-18.5
MIN YEAR	6.7	8.6	6.1	6.9	6.4
MIN MAY - OCT	17.9	18.8	17.0	18.4	16.7
MAX YEAR	-5.3	-4.4	-6.7	-5.7	-6.6
MAX MAY - OCT	5.2	5.1	3.0	5.2	2.8
MEAN YEAR	0.7	2.1	-0.3	0.6	-0.1
MEAN MAY - OCT	11.6	11.9	10	11.8	9.8
T-value		**-1.9**	**1.4**	**0.10**	**2.21**
P-value		**0.07**	**0.17**	**0.92**	**0.04**
Interpretation		**Same**	**Same**	**Same**	**Different**

These differences in climate over the three years of the study are important to consider in terms of errors in water balance estimates over the short term. The effect of differences between the long-term climate estimates and the year-to-year weather patterns experienced at the study sites may include deviations related to the colder summer season experienced in 2004, for example. Colder temperature would mean that less evaporation would have occurred at lake sites during 2004. This effect would have resulted in less water leaving the catchment via evaporation, more throughflow conditions at lake sites, and more water available for runoff. However, because the isotope model includes temperature estimates based on a thirty-year normal, the isotopic variations observed in 2004 as a result of lower temperatures would not be synchronised with temperature profile experienced during this period. However, isotope results for this study are averaged over the three-years of study, therefore lower temperatures experienced in 2004 are not anticipated to affect the model outputs for E/I estimates or water-yield. Snowfall during 2002 was also lower than long-term mean monthly values at Fort McMurray, which may have resulted in lower water-yields from catchments during spring freshet, and less water stored in lake systems. However, this effect was minimized by sampling routines, which aimed to collect isotope samples during the late summer maxima of evaporative enrichment. This practice ensured that the isotopic signal collected at the lake sites during the late fall season would represent the mean summertime patterns experienced at each lake site, and hence act to smooth out seasonal variations occurring throughout freshet as a result of the winter period snowfall patterns.

Table 1.6 Monthly rainfall, snowfall and precipitation data for the period of 1971 – 2000, and 2001 – 2004 at the Fort McMurray climate station. * = Significantly different from the long-term mean.

Type	*Month/Unit*	*Climatology 1971 - 2000*	*2001 (pre-season)*	*2002*	*2003*	*2004*
RAIN	Jan	0.5	0	0.8	0.2	0
	Feb	0.8	0.4	0	N/A	3.7
	Mar	1.6	6.2	N/A	1.9	0.9
	Apr	9.3	23	0.6	8.4	8.5
	May	34.2	41.4	19.4	39.9	49.6
	Jun	74.8	50.6	58.8	84.5	16
	Jul	81.3	56	145.9	69.9	36.5
	Aug	72.6	50.3	57.8	48.7	17
	Sep	45	26.5	36	86.2	54.5
	Oct	18.8	13.2	8.4	35.4	5
	Nov	2.4	7.8	0.7	N/A	2
	Dec	1.1	N/A	0.4	0	2.5
		T-Value	**1.41**	**0.16**	**-0.66**	**1.67**
		P-Value	**0.19**	**0.88**	**0.53**	**0.13**
SNOW	Jan	27	12.5	14.7	7.1	48.7
	Feb	20.6	15.4	11.8	31.7	20.4
	Mar	20.4	29.3	11.5	27.1	20.3
	Apr	14.5	0	9.6	1.4	14.5
	May	2.9	9	0.2	20.1	5
	Jun	0	0	0	0	0
	Jul	0	0	0	0	0
	Aug	0	0	0	0	0
	Sep	2.4	0	N/A	3.2	1.5
	Oct	13.1	6.6	21.2	18.1	7
	Nov	29	12.2	18.4	17.4	13
	Dec	25.9	18	13.3	18	24.5
		T-Value	**1.9**	**2.4**	**0.3**	**0.03**
		P-Value	**0.09**	**0.04***	**0.76**	**0.98**
PRECIP	Jan	19.3	12.5	15.5	7.3	38.3
	Feb	15	12.5	10.1	21.8	16.9
	Mar	16.1	26.5	10	25	15
	Apr	21.7	23	9.2	9.8	23
	May	36.9	50.4	19.6	52.4	54.6
	Jun	74.8	50.6	58.8	84.5	16
	Jul	81.3	56	145.9	69.9	36.5
	Aug	72.7	50.3	57.8	48.7	17
	Sep	46.8	26.5	36	89.4	56
	Oct	29.6	19.8	29.6	56.5	12
	Nov	22.2	19.4	19.1	12.9	15
	Dec	19.3	11.1	10.7	18	27
		T-Value	**2.2**	**0.4**	**-0.6**	**1.34**
		P-Value	**0.06**	**0.67**	**0.55**	**0.21**
RAIN	SUM	342.2	275.4	328.8	375.1	196.2
SNOW	SUM	155.8	103	100.7	144.1	154.9
PRECIP	SUM	465	358.6	422.3	496.2	327.3
		T-Value	**4.69**	**3.0**	**-1.2**	**2.02**
		P-Value	**0.04***	**0.10**	**0.35**	**0.18**

Testing isotope mass-balance model outputs: Three isotope mass-balance model scenarios were developed and examined to illustrate the effects of each step of model development as presented in previous studies (Gibson 2002a, Gibson *et al.* 1993a, Zuber 1983). This analysis also proved the applicability of the dual-fit model to an isotope mass-balance approach for this region. The results were examined in terms of $\delta^{18}O$ - $\delta^{2}H$ space (Figs. 1.15, 1.16) and also by a model-by-model comparison of output results (Fig. 1.17).

The first approximation (FA; shown in Fig. 1.16-1) model is the basic, open water model, following an approach applied by Gibson *et al.* (1993a) that did not flux-weight parameters such as relative humidity and temperature; instead, seasonal averages for the ice-free months are used in place of evaporation flux-weighting methods. The isotopes in precipitation are estimated using a yearly amount-weighted estimate based on modelled GNIP station data (Bowen and Revenaugh 2003). This application does not apply fitting techniques employed to calculate $\delta_{A;}$ rather, it assumes unweighted δ_A and δ_P equilibrium, and hence predicts a slope of 4, thus including an additional level of uncertainty, especially with regard to small lake systems. Gibson *et al.* (1993a) fitted C_K for deuterium, as initially proposed by Zuber (1983), to match the slope, which is now known to be a less favourable approach, especially in seasonal climates (Gibson 2002a, Gibson and Edwards 2002). For a complete discussion of the importance of calculating humidity during the open-water season, and of the relationships between δ_A and δ_P, see Gat (1995).

The evaporation flux-weighted intercept model (EFW-IM; Fig. 1.16-2) applies flux-weighted versions of the relative humidity, temperature and isotopes in precipitation. The calculation of δ_A is based on the difference between δ_P and δ_A, ϵ^*; therefore, no fitting is required, as outlined in Gibson (2002a). Amount-weighted δ_P values were used to calculate atmospheric effects and E/I ratios. These δ_P values were generated using an intercept approach where an adjusted intercept based on shallow and deep groundwater isotopic information is incorporated with values from locally collected precipitation signals (Fig. 1.9). This version of the isotope mass-balance model does not use the interpolated station data (CNIP, Bowen and Revenaugh 2003).

The dual-fit model (DF; Fig. 1.15), which was used in a study of Boreal lakes (Gibson *et al.* 2002), employs a fitting technique based on the latitude coordinates of each lake system and a slope factor to estimate δ_A. The DF model represents more advanced approach that incorporate specialized weighting, new model equations and fit techniques (Gibson *et al.* 2002, Horita and Wesolowski 1994). Flux-weighted relative humidity and temperature estimates are used; however, amount-weighted isotopes in precipitation are applied to calculate the E/I ratio (using the Bowen and Revenaugh 2003 data).

Results shown in Figure 1.16-1 and 1.16-2, illustrate a fluctuating δ^* value based on the technique of deriving δ_A. The FA (Fig. 1.16-1) model has poorly aligned δ^* values, indicating the weakness in model structure linked to this measurement. In this model, for example, the δ_A estimate relies on a non-weighted seasonal model and derives the estimates of δ_A based on the difference between ϵ^* and δ_P. This assumes that equilibrium is being achieved and does not account for the seasonal effects that are found in natural systems owing to evaporation occurring during the warmest periods of the open-water season. When equilibrium effects are not accounted for, the δ^* values will fall below the lake isotopic signals, and the model will fail to accurately represent the natural world. In the EFW model (Fig. 1.16-2), the evaporation flux-weighting is accounting for some of the effects found in equilibrium, however this model does not obtain the predicted result for δ^* (Fig. 1.3) because equilibrium conditions are not fully achieved. Whether this is because the relative humidity estimates are not sensitive enough to represent humidity conditions occurring at the open-water lake sites, or whether the evaporation effects by which the systems is being weighted towards have not been estimated properly, this model is not finely-tuned enough to account for all equilibrium effects. Thus, the final version of the model applies the dual fit approach (shown in Fig. 1.15) to calculating δ_A and therefore aligns δ^* in the proper location as an extension of the lake water isotopic signatures. This allows for proper accounting of equilibrium effects in nature. Further study to improve estimates of climate variables will allow for accounting of equilibrium effects that could generate a more sensitive estimate of δ_A and δ^* and apply the use of the EFW approach in the model.

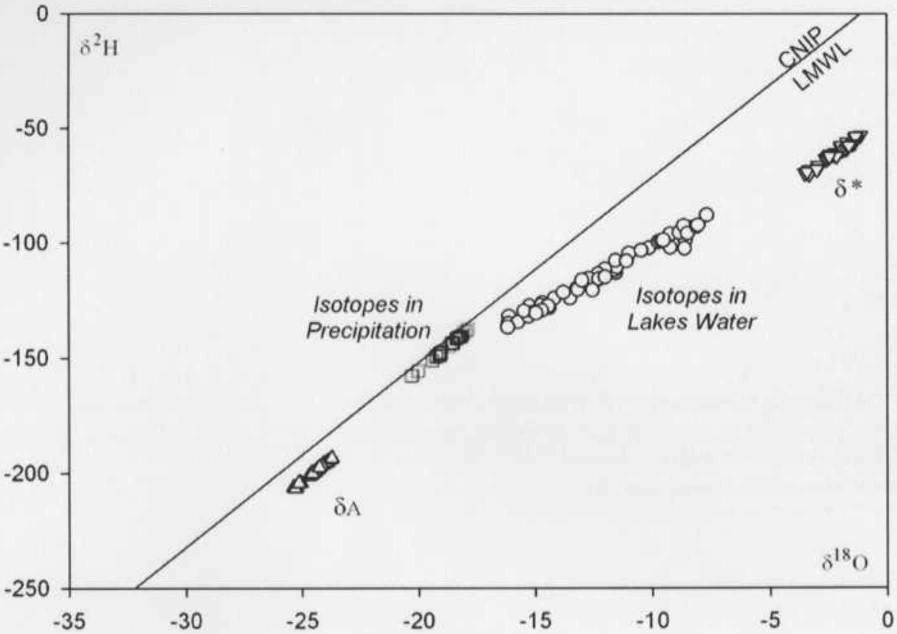


Figure 1.15 The final version of the isotope model where equilibrium conditions have been met by applying a dual fitting (DF) approach. Results are illustrated in terms of the isotopes in lake water (circles), isotopes in precipitation (amount-weighted values; open squares), isotopic composition of the atmosphere (δ_A; upward triangles), and the limiting isotopic composition of the system (δ^*; downward triangles). See text for further information.

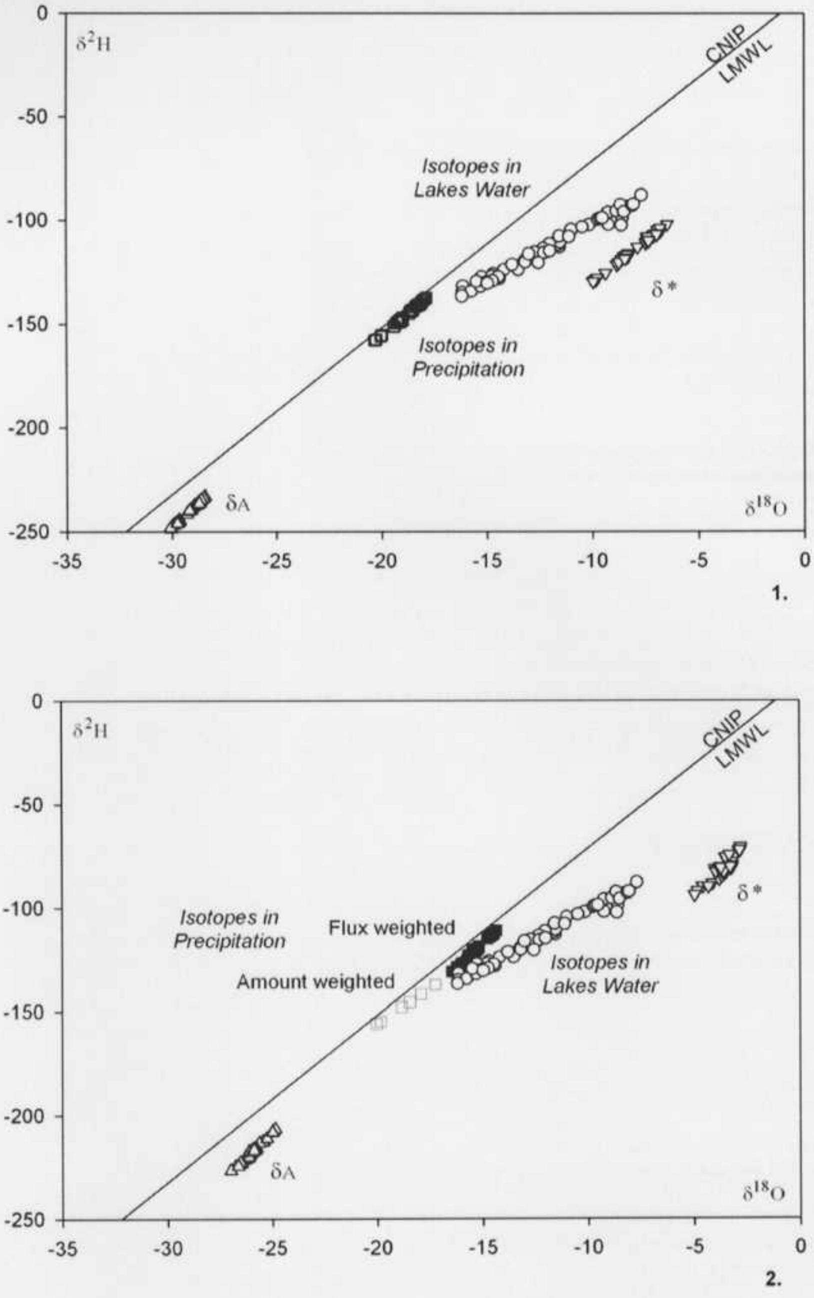


Figure 1.16 Layout of the first two isotope mass-balance model results, box 1 shows the first approximation (FA) version, box 2 shows the evaporation flux-weighted version (EFW) of the model approach. Results illustrated in terms of the isotopes in lake water (circles), isotopes in precipitation (amount-weighted values; open squares), flux-weighted values in precipitation (closed, dark squares), isotopic composition of the atmosphere (δ_A; upward triangles), and the limiting isotopic composition of the system (δ*; downward triangles). See text for more details.

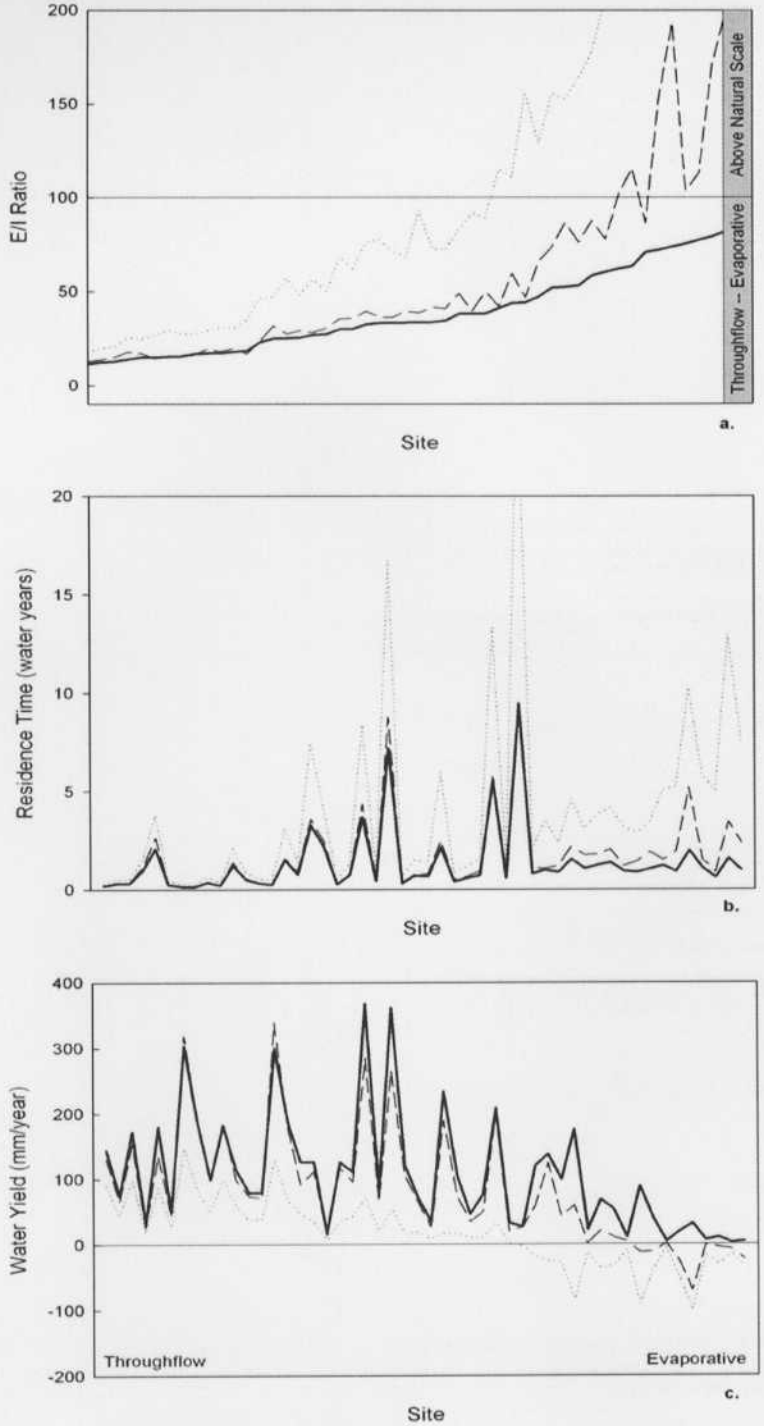


Figure 1.17 E/I output (a), residence time (b) and water-yield (c) are shown for the three isotope mass-balance model scenarios. The first approximation (FA) model is given by the dotted line, the long-dashed line indicates the evaporation-flux weighted intercept model (EFW-IM) and the solid, dark line illustrates the dual-fit model (DF). Findings are ordered based on the results of the DF model output for E/I.

In Fig. 1.17, the exaggerated model output values for all three parameters illustrate the effect of miscalculating for equilibrium. The DF model best approximates the E/I ratio, while the EFW-IM model also provides a reasonable estimate; however the FA model results become more inaccurate as the lake systems progress from a throughflow (low E/I ratios) to an evaporative state. Residence time and water-yield are also best approximated by the DF model, while the EFW-IM results fall close to the DF estimate again. The FA model gives unreasonable residence times for some of the lakes found within the mid-range of the E/I scale. Water-yield results for the FA model trend toward negative values above E/I ratios of 40% (based on the DF order) for the FA model, but hold reasonable approximations for water-yield below these numbers at the throughflow end of the E/I spectrum.

Sensitivity Analysis

Once the scenario analysis determined the most reasonable isotope mass-balance model to apply and an indication of the estimates that could be expected, sensitivity analysis was undertaken to determine how data variants within the model affected the output results in terms of E/I. The sensitivity or responsiveness of a system is key to determining how the model operates in terms of variations of input data when multiple data sources are available, and in terms of the breadth that a model can handle when faced with input errors. Measuring and understanding how climate variables react within the model framework will help direct effort towards more accurate estimation of the most sensitive climate variables. Thus specific targets can be generated to determine an acceptable level of error for this model.

In this study, a number of methods were applied to i) define the isotope mass-balance model input climate variables that were most responsive (within the framework of model output) to variations in their values compared to a base output data set, ii) determine the influence and impact of flux weighting on model variables and iii) define model sensitivity in terms of output E/I. These three approaches allowed for assessment of isotope mass-balance model input factors, examination of the influence of specialized flux weighting approaches on isotopic parameters and climate variables, and consideration of the sensitivity of the E/I ratios to a range of isotopic enrichment factors.

Testing Model Input Factors: Simulations were developed to determine how variations on the climate data (see Table 1.4) would impact model results. A base case data set was derived using the best-known climate and physical factors as explained previously in this chapter. This base case data set was different from the base case used in the final model, as it was derived at an earlier junction in the work-up of climate data. The base case model applied the following data sets: temperature (CRU10", SD 0.7, avg 10.8°C), precipitation (CANGRID, SD 42, avg 475 mm), evaporation (CRU0.5° Hamon, SD 12.7, avg 480 mm), and relative humidity (CRU10", 0.6, avg 69%), all of which were tested for their appropriateness in this analysis, as described earlier. Tested data sets are listed, including their average and standard deviation (Table 1.7), and the raw and percentage differences from the base case (Table 1.8).

Table 1.7 Data sets employed (see Table 1.4 for specifications of each climate data set) in the model testing. The variation type applied in testing, standard deviation and average values are given for each of the tested data sets.

Model Input	*Model Variation*	*Variation Type*	*SD*	*Avg*
Temperature	Temperature 1	CRU0.5	0.5	10.9
	Temperature 2	ANUSPLIN	0.8	10.6
	Temperature 3	IDW	0.5	11.0
	Temperature 4	NCEP	0.6	9.6
		BASE CASE	**0.6**	**11.5**
		ALL	**0.6**	**10.7**
Precipitation	Precipitation 1	ANUSPLIN	40	470
	Precipitation 2	CRU0.5	36	413
	Precipitation 3	CRU10	25	555
		BASE CASE	**42**	**475**
		ALL	**36**	**478**
Evaporation	Evaporation 1	Hamon CRU10	16.6	498
	Evaporation 2	ECMWF	19.2	442
	Evaporation 3	Hamon NCEP	15.6	441
	Evaporation 4	CGCM2_A22	8.4	522
		BASE CASE	**13**	**480**
		ALL	**15**	**476**
Relative Humidity	Relative Humidity 1	NCEP (surface)	1.3	80%
	Relative Humidity 2	ECMWF	1.1	63%
		BASE CASE	**0.6**	**68%**
		ALL	**1.0**	**70%**

The relationships as presented in the table above indicated that a statistical measure to identify differences in output based on the input data variations was required. Therefore, output results were also analysed for differences in means (Student's *t*) between the base case and the variants for output results, after the appropriate transformations were applied to normalize data. Results indicated that threshold levels, as defined by the point at which statistical differences occurred between the base case and the test case, existed for evaporation, precipitation and relative humidity deviations. Table 1.8 shows the outputs for E/I ratios for the specific models.

Temperate was not sensitive to shifts in its data input; and was the only climate variable for which all data sources could be applied with relatively little effect on the output results (~1.5% change, Table 1.8); even with simulated shifts to temperature of +10°, alterations were not found between means of E/I ratios. Evaporation also did not appear sensitive, and results for all data tested were not significantly different than the base case, even where data sets differed from the base case by 42 mm on average per year (CGMC_A22) Percentage difference based on new evaporation input data between the base case E/I and E/I outputs sets was a maximum of 0.5%.

The CRU10" precipitation data set was significantly different from the base case (T-value = -2.27, P = 0.03) for E/I ratios; this data set was separated from the base case by 80 mm on a yearly average, suggesting that this may be a threshold value for precipitation deviations from means. However, all other gridded precipitation data sets analysed fell under this deviation. The NCEP relative humidity was not different from the mean base case (T-value = -1.90, P = 0.06) data set for E/I ratios, but as the P-value was just under the 95% criteria, it is possible that this data set may be close to the threshold value. The NCEP data set deviated on average 12% from the base case (average values of 81% compared to 69%); using these criteria the Hadley GCM3 data relative humidity (average 87%) estimates would have failed significance testing. Precipitation and relative humidity data sets were the most sensitive in terms of the climate variables, with percentage differences between the base case on the order of 1 - 15% for E/I (Table 1.8).

Precipitation data was sensitive (see Table 1.8, variation up to 6.5% were observed in E/I ratios) because of the structure of the model used for calculating this analysis. This model applied a monthly amount-weighted feature to account for impacts to isotopes in precipitation that occurred as a result of increased precipitation. The final version of model, therefore, did not include the monthly amount-weighted isotopic signal and instead relied upon a version of the data averaged and amount-weighted for the year (Bowen and Revenaugh 2003). Because this feature was not included in the final version of the model, the observations for precipitation data noted in this analysis is not considered to be reflective of the sensitivity of the model and are therefore disregarded.

Table 1.8 Differences between the raw data values and the base case data, the percentage differences and the weighted percentage difference from the base case.

Factors	*Version*	*Diff BC-x*	*% Diff BC-x*	*E/I %*
Temperature (°C)	Temp1^{tr}	-0.6	+5%	0.4%
	Temp2^{tr}	-0.9	+8%	0.6%
	Temp3^{tr}	-0.5	+4%	0.4%
	Temp4^{tr}	1.9	+16%	1.3%
Precipitation (mm)	Precip1^{tr}	-4.9	1%	15.4%
(Final model)	Precip2^{tr}	-62.0	13%	10.7%
	Precip3^{tr}	+80.0	-17%	40.8%*
Evaporation (mm)	Evapo1^{tr}	-18.4	-4%	0.1%
	Evapo2^{tr}	+37.7	8%	0.2%
(Final model)	Evapo3^{tr}	+38.8	8%	0.4%
	Evapo4^{tr}	-42.1	-9%	0.2%
Relative Humidity (%)	RH1^{tr}	+12	-18%	70.0%$^{+}$
	RH2^{tr}	-4	6%	4.8%

* significantly different from base case
$^{+}$P = 0.06
^{tr} = transformed

This simulation using variable sources of input climate data suggests that the isotope mass-balance model is highly robust in terms of E/I ratios. It is anticipated that residence time and water-yields outputs would be more sensitive than the E/I ratios, although this remains to be tested. Climate data input variations only affected output at high levels for both temperature and evaporation, indicating a wide buffer is available for errors in these climate data sets. Precipitation was affected in this version of the model due to the inclusion of an amount-weighting technique that was not applied in the final version of the model. Relative humidity, therefore, remains the most sensitive climate variable to input sources, with input variants of 18% approaching significance levels. Some data sets (NCEP and Hadley GCM3) were not appropriate to use as estimates of relative humidity in this model, although this was apparent well before testing of parameters provided statistical evidence. Model outputs fluctuated up to a maximum 15% for reasonable variations of climate input. The use of a base case test model to determine sensitivity between variables may be problematic because there is no true correct data value for the model and therefore the difference between the base case may not be significant even when a statistically proven difference is shown. This concern was addressed by applying a different method of sensitivity analysis, described in the following paragraphs.

Testing Flux-Weighting Approaches: The flux-weighting approach allowed for model fitting based on the open-water evaporative conditions occurring at each lake site (Gibson 2002). The influence of evaporation flux weighting was explored through examination of the direct impact of flux weighting, based on results of applying different input evaporation data scenarios to the flux-weighted variables of temperature (Fig. 1.18a), relative humidity (Fig. 1.18b), and isotopes in precipitation ($\delta^{18}O$ and $\delta^{2}H$, shown in Figs. 1.19a and b, respectively). Three different data sets were chosen for comparison, as well as a non-flux weighted seasonal version of the factors. The three options selected for analysis, namely, the Hamon-based CRU 0.5° (referred to as the base case in Fig. 1.18), the CRU 10" gridded climate data and the European Centre for Medium Weather Range Forecasts (ECMWF) global climate model (GCM) data were used to illustrate the impact of flux-weighting to climate input, based on a range of reasonable estimates for evaporation. The ECMWF and the Hamon NCEP (used in the final version of the isotope mass-balance model) evaporation estimates had similar data ranges, with the exception that the Hamon NCEP data set deviated toward lower evaporation occurring at higher latitudes (similar to the Hydrological Atlas of Canada data), while the ECMWF tended toward a slight increase at the higher latitudes. The diagrams below (Figs. 1.18 and 1.19) illustrate findings for each approach and results for factors tested (temperature, relative humidity and the isotopes in precipitation) as a pulse line through the data result at individual lakes sites.

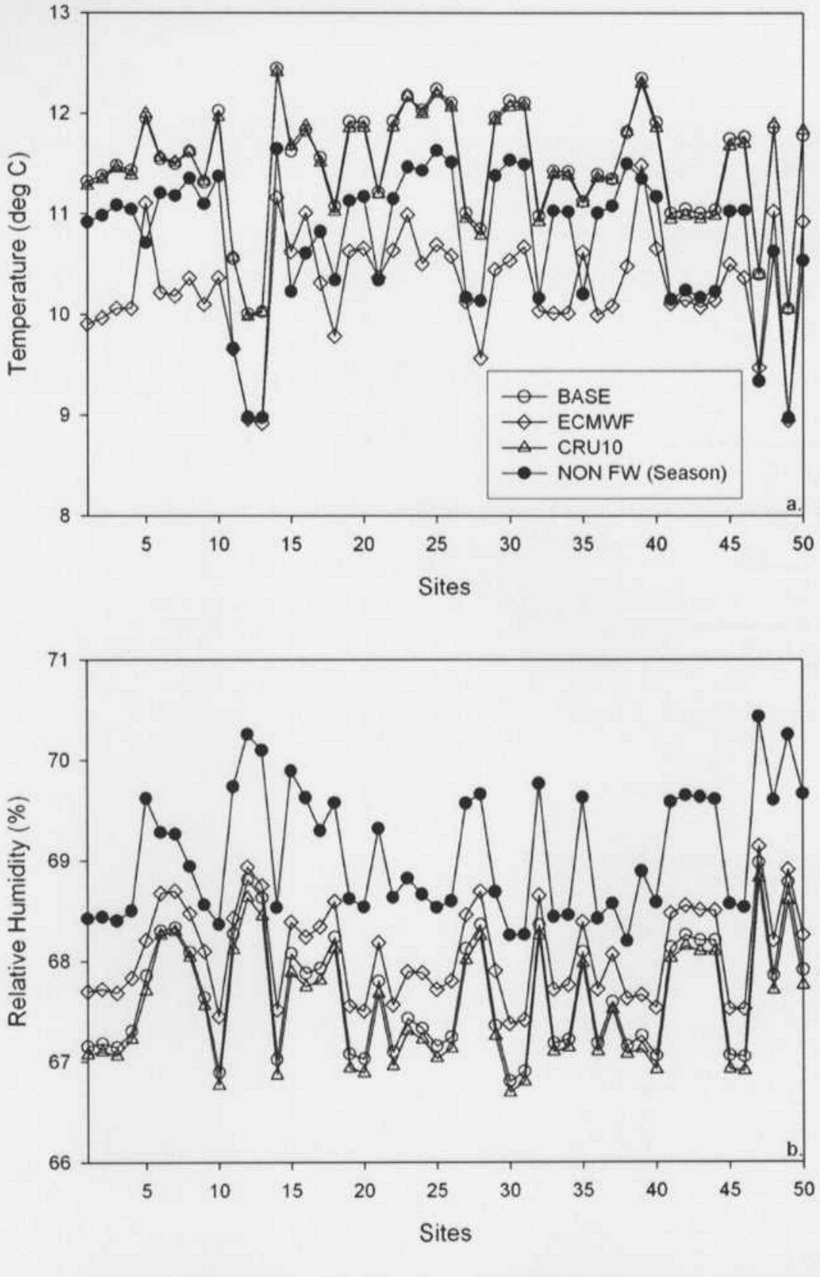


Figure 1.18 Pulse diagram illustrating temperature (a) and relative humidity (b) data sets for lake sites (n = 50) flux-weighted by several evaporation data sets. Base case (CRU 0.5°) is given with open circles, open triangles illustrate the CRU 10" data set, the ECMWF climate data are shown with open diamonds, and the closed circles are the non-flux weighted average seasonal values (May to October). Table 1.4 lists the climate data sources applied in this analysis.

The influence of flux weighting on temperature (Fig. 1.18a) resulted in variation over approximately 1.3° given different flux-weighting approaches. The maximum within-data set standard deviation is 0.70; therefore, this variation is not considered to be significant (see Knoller and Strauch 2002 for reference to this approach). The non-flux weighted data set occurs at the median position between the CRU scenarios and the ECMWF data. Depending on the lake site, flux weighting may have almost no effect if the ECMWF climate data were applied to temperature. The impacts of flux weighting on temperature using the base case and the CRU 10" data set are very similar, showing almost complete heterogeneity across estimates at study lakes. However, because temperature is not a highly sensitive variable, the impact of using different flux-weighting scenarios to weight temperature is not considered to be significant (see discussion in next section).

Relative humidity, on the other hand, is a sensitive variable, as explored in the next section, which describes the sensitivity analysis (Fig. 1.20). The non-flux weighted relative humidity seasonal estimates are higher than the flux-weighted versions based on both the CRU and the ECMWF scenarios. Therefore, the evaporation flux weighting has the impact of reducing relative humidity for all lake sites to below mean open water or annual averages. The ECMWF data represents a moderate estimate of relative humidity, and the CRU data sets result in lower relative humidity estimates, compared to the ECMWF approximations. Both CRU data sets result in similar average values of relative humidity, with ~0.5° of variation between them. Average variations of 1.5%, which occur across these data sets, should not have an impact on isotope mass-balance model output for E/I ratios (see above section), although may affect water-yield and residence time. The maximum standard deviation found within these three data sets is 0.60, which is less than half the variation observed between different data sets.

The isotopes in precipitation vary by 1‰ for $\delta^{18}O$ (Fig. 1.19a), and by ~5-10‰ for $\delta^{2}H$ (Fig. 1.19b), which are close to standard deviations for these data sets (0.5‰ and 5‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively). The non-flux weighted δ_P signal is slightly higher than the CRU estimates, and the ECMWF flux-weighting scenario impacts the estimates by making them more negative, resulting in more depleted input precipitation isotope signals.

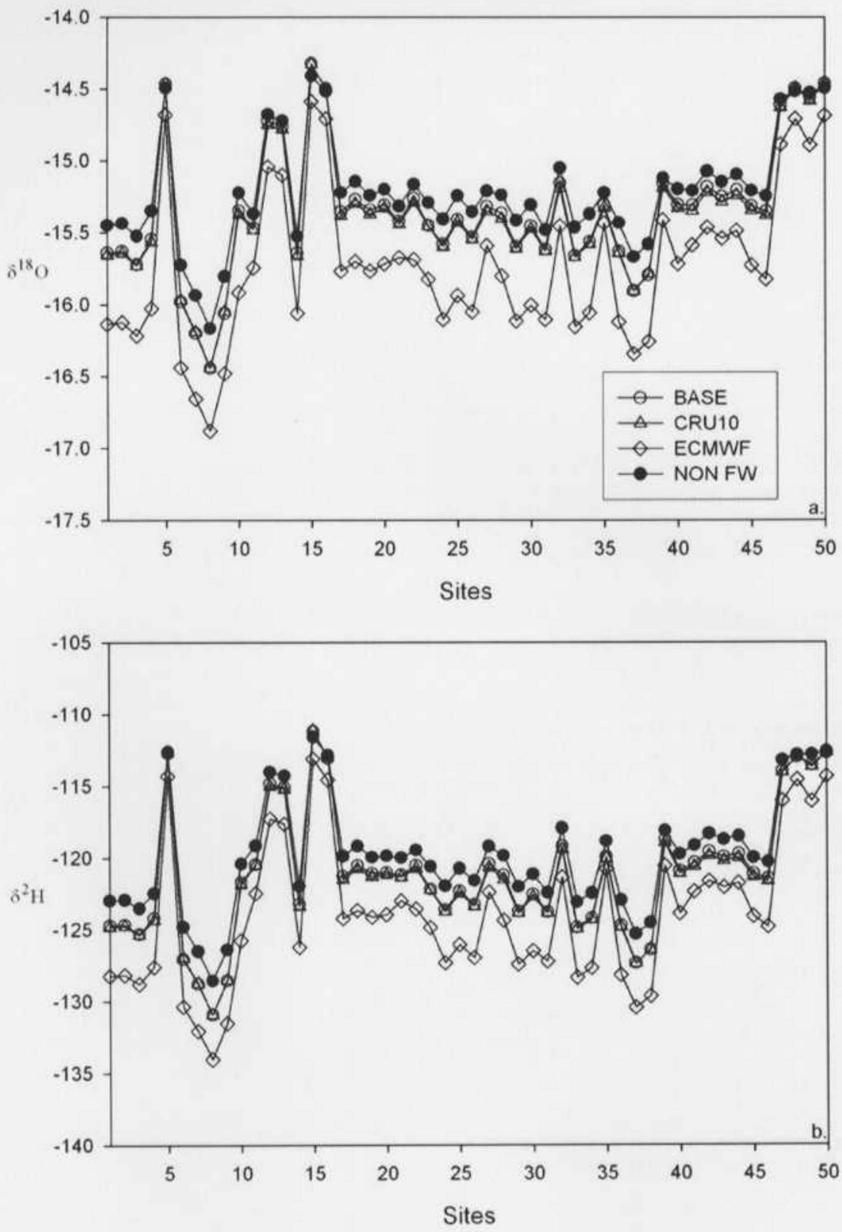


Figure 1.19 Pulse diagram illustrating δ^{18}O (a) and δ^2H (b) data sets for lake sites (n = 50) flux-weighted by several evaporation data sets. Base case (CRU 0.5°) is given with open circles, open triangles illustrate the CRU 10' data set, the ECMWF climate data are shown with open diamonds, and the closed circles are the non-flux weighted average seasonal values (May to October).

Testing Sensitivity by Isotopic Flux: Sensitivity analysis was conducted to examine the response of factors in the E/I equation across a range of hydrologic conditions, following the methods outlined in Gibson *et al.* (1993a). In analysis of E/I ratio sensitivity, volumetric lake drawdown (dV/dt), relative humidity (rH), isotopic composition of the atmosphere (δ_A or dA), isotopic composition of precipitation (δ_P or dP), temperature and latitude were considered. Lake reduction was generated by a non-steady sensitivity test simulating the effect of a 5% drawdown, whereas relative humidity, temperature and δ_P were altered in relative proportions by +/-5%, latitude by +/-5 degrees, and δ_A was shifted by 5% (based on an ε^* fractional amount, which has a hypothetical value of 1 but is adjusted to limit E/I differences between $\delta^{18}O$ - δ^2H). These altered data were compared to a base case scenario to determine the percent change across the ranges of variability. Fig. 1.20 illustrates the error in E/I ratios for oxygen-18 that occurs along a continuum of isotope signatures from –18‰ to –7‰, which represents theoretical isotopic enrichment in lake systems across a regional study zone such as those examined in this research project, or that may occur over time in one particular reservoir.

At the throughflow end of the scale (more negative $\delta^{18}O$ values), reservoir drawdown (dV/dt) and δ_P (dP) exhibit high sensitivity. In the case of dV/dt, this relationship however, is unlikely to be observed in nature because reservoirs with high throughflow do not change in volume to this degree. Reservoirs that exhibit throughflow conditions equal to those modelled in this exercise would be best analysed by a non-steady state isotope mass-balance model, and thus are known to be poorly represented by this steady-state modelling approach (Gibson and Edwards 2002). As a reservoir decreases in volume over time more evaporation will occur (higher E/I ratios) as a result of higher maximum water temperatures, latent heat loss and air-water boundary layer effects (Oke 1978). As shown in Fig. 1.20, as more evaporation occurs, less error is incurred in the modelled output values (E/I). Isotopes in precipitation are also more sensitive in throughflow lake systems, and steadily progress to just less than 100% error, at –18‰ $\delta^{18}O$, under conditions of increasing and decreasing δ_P values. Throughflow reservoir systems with low E/I ratios will be sensitive to increases and decreases in the isotopic composition of precipitation. At high isotopic enrichment levels, δ_P is not considered to be sensitive (~+/-10%).

The remainder of the factors show low sensitivity under throughflow conditions, and higher sensitivity at the evaporative end of the hydrologic spectrum. Relative humidity (rH) shows higher sensitivity, increasing to almost 25% in the positive direction, and decreasing to below 20% in the negative direction. This result indicates that E/I calculations are more sensitive given higher relative humidity values over lower relative humidity. Latitude (not shown) has higher sensitivity with increasing evaporative conditions; this simply indicates that a shift toward higher latitudes would increase sensitivity and errors, as is known to be the case for northern sites (Gibson *et al.* 1996). Temperature is not very sensitive, and increases in temperature do not affect the E/I ratios (not shown). Sensitivities for low levels of isotopic enrichment are also constrained in part by the analytical uncertainty (Gibson 1993).

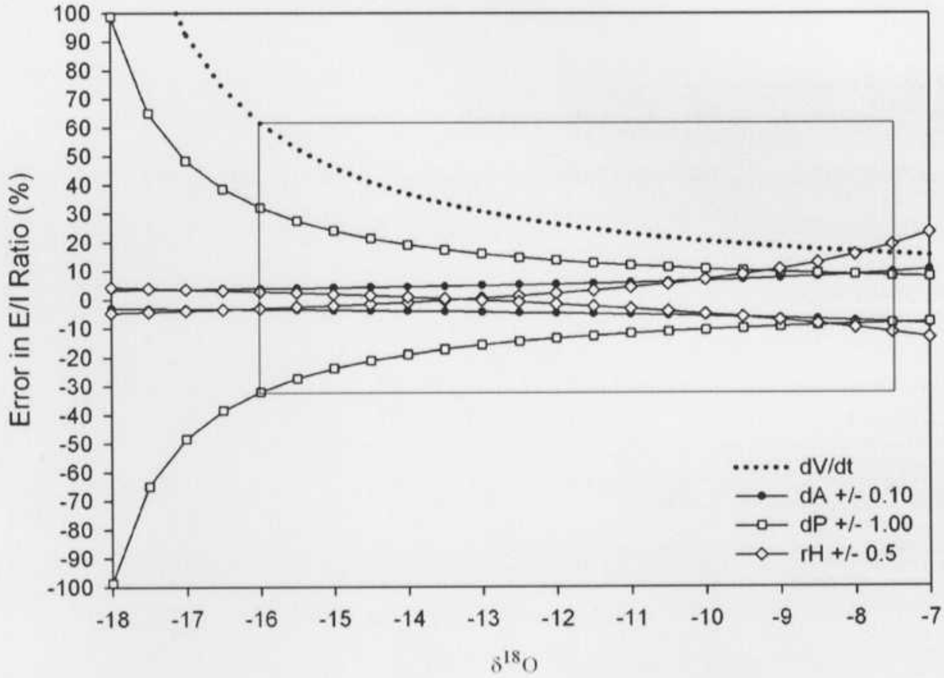


Figure 1.20 Error in E/I ratios (%) for a range of isotopic conditions. The resulting change is shown here as the percentage difference in E/I ratios between a base case and the new case in E/I factors as, the percentage change of reservoir drawdown (dV/dt, the change in volume over the change in time) is shown with the dotted line, δ_A, atmospheric enrichment (as a fraction of e*, base case +/- 0.05) is illustrated with small black circles on a solid line, relative humidity (base case +/-5%) is given with the diamonds on a solid line, and δ_P (base case +/-5%) is shown with squares on a solid line. The box illustrates the range of values found in this study.

Overall, model sensitivity is isolated to the factors of isotopes in precipitation and relative humidity. Lake water isotopic results in this model are constrained to approximately –16‰ and –7.5‰ (shown by the box in Fig. 1.20); therefore, errors associated with throughflow conditions above these values are outside the range of lake systems found in the northern Alberta. As a result, no errors greater than ~60% (volumetric drawdown) or ~32% (isotopes in precipitation) will occur at low isotopic enrichment. At high levels of isotopic enrichment and concurrent increasing relative humidity, the model is sensitive to shifts in relative humidity on the order of 25%. It is interesting to note that isotopic conditions associated with the liquid water phase in lakes and precipitation samples are more sensitive in this isotope mass-balance model than are the variables representing environmental conditions of relative humidity, temperature and atmospheric isotopic shifts. Given these results, and what is known about the low expectancy for throughflow conditions to occur at the same time as reservoir drawdown, errors associated with this model are projected to be on the order of ~30%.

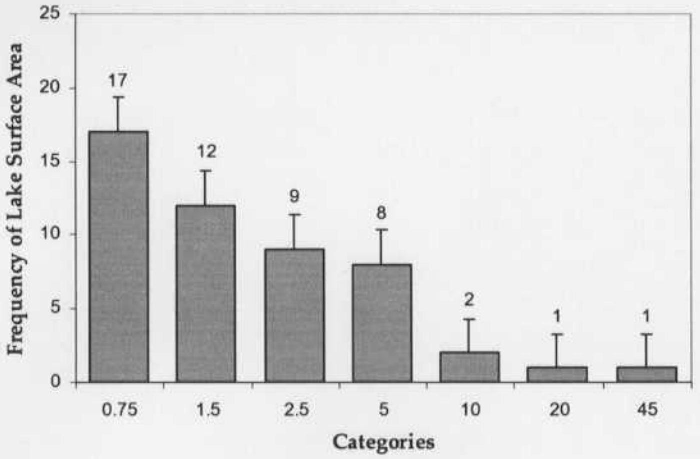
Regional Scale Implications for Boreal Plains Hydrology

Study catchments and lakes vary in aerial extent, depth, volume, elevation, slope, and drainage ratio (DR) characteristics. Table 1.9 lists the average values and standard deviations for select basin features in regional zones. The lakes are found across a wide latitudinal gradient (see Fig. 1.4): systems in the Stony Mountains are located around 55°N, while Shield lakes located north of Lake Athabasca near the border of the NWT are closer to 60°N. Longitudinal gradients extend over ~2°, from approximately 110 to 112°W. Compared to a survey of 355 lakes in the regional area (WRS 2004), study lakes were smaller in aerial extent and drainage basin area (DBA, Table 1.9), likely a result of sample-site selection bias toward acid-sensitive systems (RAMP 2004). Lakes are smallest (based on lake area, max depth and volume) in Regions 1–3 and larger in Regions 4–6. Catchments are also larger in Regions 4–6 compared to Regions 1–3. Slopes also tend to be lower in Regions 1–3 and higher in Regions 4–6. Lakes in Region 2, 4 and 5 are found at higher elevations than the lake systems in Region 1 and 3. Drainage ratios (DR) are below the data set average in the mountainous regions of Stony, Birch and Caribou Mountains, whereas the low-lying areas, including NE and West Fort McMurray, have higher drainage ratios. The Shield systems have the highest drainage ratio of all regions.

Table 1.9 Average site characteristics for lakes by region. Standard deviations are reported in brackets below average values. Data set average, standard deviation (SD) and standard mean error (SE Mean) are provided.

Region #	*Lake Area (km^2)*	*DBA (km^2)*	*Max Lake Depth (m)*	*Lake Volume (mm)*	*Lake Elevation (masl)*	*Slope Max (°)*	*Slope Mean (°)*	*DR*
1	1.7	21	1.8	1031	521	20.6	1.2	24
	(2)	(20)	(0.6)	(136)	(105)	(12)	(0.5)	(18)
2	1.4	12	1.9	886	697	23.5	1.8	9
	(0.6)	(6)	(0.7)	(307)	(49)	(8)	(0.6)	(6)
3	1.1	17	1.5	821	525	14.4	1.3	26
	(1)	(15)	(0.3)	(262)	(84)	(7)	(0.9)	(14)
4	6.9	39	5.9	2243	709	33.1	2.9	15
	(13)	(45)	(8)	(3219)	(61)	(16)	(1.3)	(10)
5	3.3	28	6.7	4121	881	20.9	2.9	11
	(4)	(17)	(6)	(2934)	(25)	(5)	(0.8)	(5)
6	1.5	58	13.6	3688	308	47.7	3.9	48
	(1)	(56)	(8)	(2003)	(20)	(19)	(0.6)	(47)
Average	2.8	27	4.3	1810	613	26	2	20
SD	7	32	6	2144	167	15	1	21
SE Mean	0.9	4.5	0.8	303	23.7	2.1	0.2	2.9

The frequency distributions (Fig. 1.21) illustrate the prevalence of small lake systems, watersheds and drainage ratios found within this data set, which is reflective of distributions found within the 355-lake data set (WRS 2004). Small drainage ratios may increase susceptibility of aquatic ecosystems to atmospheric loading (Schindler 1976); however, values in the Stony Mountains (9), while low, will probably not exceed terrestrial supply (Shaw *et al.* 1989), owing to the large amount of vegetation (wetlands) located in that region. Drainage ratios in this data set are correlated with E/I ratios (r^2 = 0.42, $P < 0.05$), indicating a strong link between the drainage ratio and hydrologic status of lakes in these watersheds.



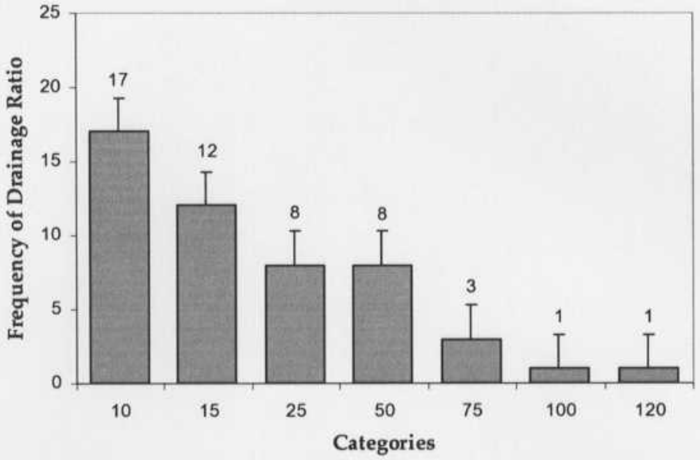


Figure 1.21 Histograms of physical parameters, including lake surface area and drainage ratio (drainage basin area/lake area). Data intervals are based on seven categories (for small samples) determined using rounded Jenks distributions. . Numbers above columns show the frequency count and error bars show the standard error for each category. Note the prevalence of lakes with smaller surface areas and drainage ratios in this data set.

Precipitation values range from 355 mm·yr^{-1} at the Shield lakes to approximately 460 mm·yr^{-1} in the Stony Mountains, while evaporation values have a smaller range, from 450 mm·yr^{-1} in the Caribou Mountains to 485 mm·yr^{-1} in the Stony Mountains (Table 1.10). Precipitation minus evaporation is negative in this region, and results decrease along a north-south latitudinal trend, with smaller values of precipitation and evaporation occurring in the north. These climate estimates are similar to information provided by the Hydrologic Atlas of Canada, which reports precipitation and evaporation values between 400 and 500 mm·yr^{-1}. Runoff ratios derived via the isotopic mass-balance method are also similar to those derived from the Hydrologic Atlas of Canada data, which range from 0.1 to 0.50 (Environment Canada 1978). Temperature and relative humidity are variables that are fairly consistent throughout the study sites. Temperature does show minor variations, with slightly higher temperatures occurring in the sites northeast of Fort McMurray, and slightly lower temperatures in the Caribou Mountains. The Shield lakes, while located relatively far north, may be warmed slightly by the microclimate influence of nearby Lake Athabasca.

Table 1.10 Climate data results for regional areas.

Region #	*Precipitation (mm)*	*Evaporation (mm)*	*Temperature (°C)*	*Relative Humidity (%)*
1	417	434	12.02	0.67
2	461	449	11.43	0.67
3	435	451	11.90	0.68
4	397	451	11.08	0.68
5	365	438	10.21	0.69
6	355	402	11.81	0.68
Average	413	441	11.5	0.68
SD	36	16	0.6	0.005
SE	5.2	2.2	0.08	0.0008

Regional averages for isotopic data are given in Table 1.11 for both oxygen-18 and deuterium for field-collected lake water, and Bowen and Revenaugh (2003) isotopes in precipitation. Results are also shown for the three main outputs from the isotopic mass-balance model ($\delta^{18}O$ only): E/I ratios, water-yield and residence time. The field-collected lake water isotopic signatures ($\delta^{18}O$) range from –7 to –16‰, with a data set average of –12‰. The Stony Mountains and West Fort McMurray regions have similar isotopic averages for $\delta^{18}O$, while NE Fort McMurray, Birch and Caribou Mountains have similar isotope signals for $\delta^{18}O$. The Shield has a different isotopic signature, perhaps owing to its location and proximity to Lake Athabasca. The isotopes in precipitation, in comparison to lake isotopic signatures, have a narrower range: the southern systems are close to –18‰, while the more northern Birch, Caribou and Shield lakes fall between –19 and –20‰ for $\delta^{18}O$ values.

Table 1.11 Average regional isotope results from isotopic mass-balance model, including mean water-yield and residence time. Standard deviations are given in brackets. Data set average, minimum, maximum, standard deviation (SD) and standard error (SE) of the mean are given below.

Region #	*Isotopes Lake Water Mean $\delta^{18}O$*	*Isotopes Precipitation Mean $\delta^{18}O$*	*E/I $\delta^{18}O$ Mean (%)*	*Water-yield Mean (mm)*	*Residence Time Mean (water year)*
1	-13.2	-18.4	25	96	109
	(2.5)	(0.2)	(17)	(45)	(73)
2	-9.9	-18.3	48	82	178
	(1.4)	(0.2)	(15)	(39)	(89)
3	-9.4	-18.2	55	23	183
	(1.4)	(0.1)	(16)	(15)	(54)
4	-13.1	-19.1	28	168	251
	(2.0)	(0.2)	(16)	(127)	(402)
5	-14.4	-20.2	25	186	336
	(1.8)	(0.2)	(12)	(70)	(122)
6	-13.8	-19.1	24	80	430
	(1.5)	(0.2)	(10)	(48)	(402)
Average	-12	-19	35	105	221
Minimum	-16	-20	8	5	29
Maximum	-8	-18	75	394	1320
SD	2.6	0.6	19	86	245
SE Mean	0.4	0.09	2.7	12	35

E/I ratios for the entire data set are illustrated in Fig. 1.22. The observed trend toward a higher frequency of low to moderate E/I ratios (throughflow) occurring within lake systems reflects the pattern found in lake areas, catchments areas and drainage ratios. E/I ratios are similar among NE Fort McMurray sites, and in Regions 4–6 (Table 1.11). The Stony Mountains and West Fort McMurray are the most evaporative sites based on E/I ratios alone. Water-yield varies among regions: systems in Region 3 have the lowest water-yield; followed by the Shield lakes (6), Stony Mountains (2), and NE Fort McMurray (1). The Birch and Caribou Mountains have the highest water-yields. None of the average water-yield estimates extend over 200 $mm\cdot yr^{-1}$. Residence time also varies among regions: lakes in NE Fort McMurray have the shortest residence times, followed by Stony Mountains and West Fort McMurray. The Birch Mountains, Caribou Mountains and Shield lakes have longer average water residence times.

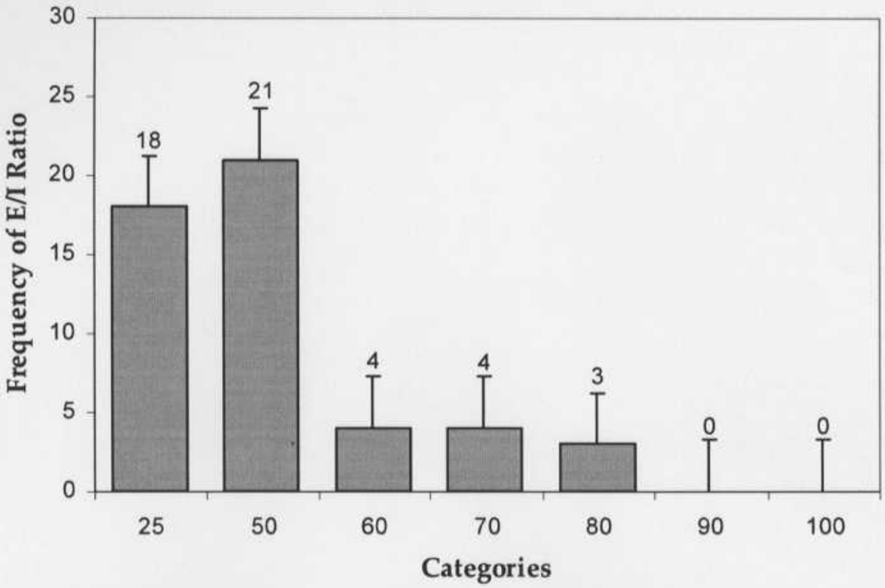


Figure 1.22 E/I ratios for 50-lake data set. Numbers above columns show the frequency count and error bars denote the standard error for each category. Note the trend toward lower E/I ratios, indicating the prevalence of regional lake hydrology toward low to moderate E/I ratios (more throughflow lakes). This is reflective of the relationships found in this data set (see Fig. 1.21) and in a broad study of 355 lakes (WSC 2004) that represent similar trends toward small lake surface area and drainage ratios, suggesting that these types of lakes are dominant in this region.

Fig. 1.23 illustrates the final model in $\delta^{18}O$-δ^2H space. The system end members, namely δ_E, δ^* and δ_A, are distributed proportionally to lake water ranges: δ^* falls along the extended LEL; δ_A is found below the LEL at approximately 200 degrees to the intercept of the LEL and the LMWL (CNIP); and the δ_E range is found along the extension of the LEL beyond the MWL. All end members are located in expected positions within $\delta^{18}O$ - δ^2H space (Gibson *et al.* 2002). Discussion of these results is continued in the next section of this chapter.

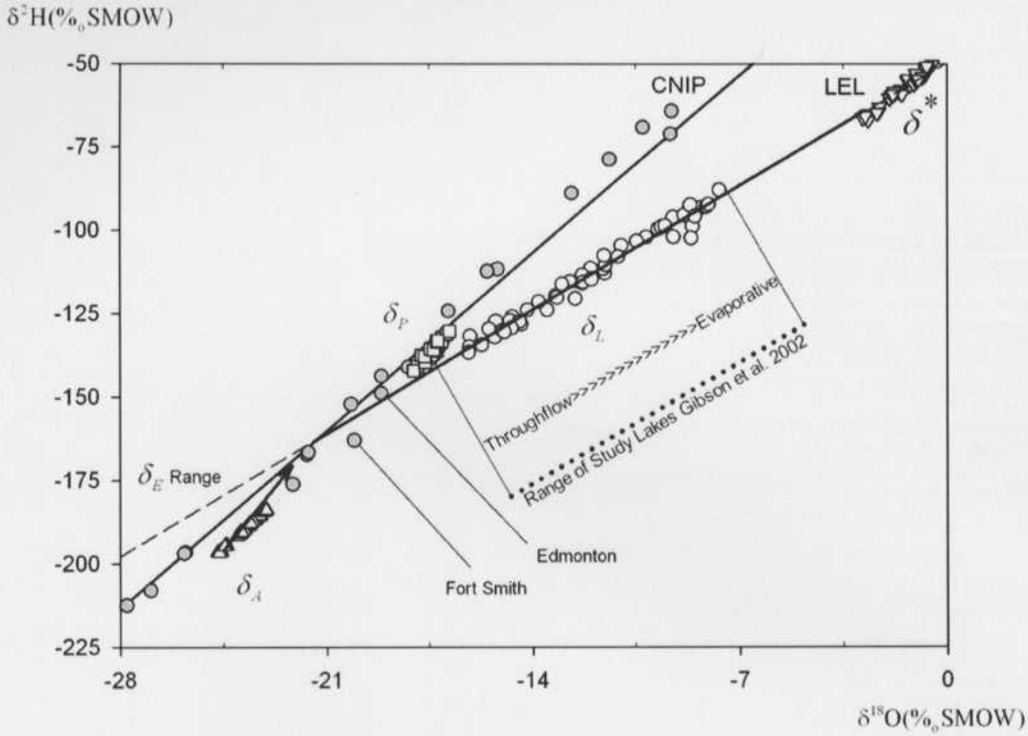


Figure 1.23 Field-collected and model-derived isotopic information from the isotope mass-balance analysis in $\delta^{18}O$ - $\delta^{2}H$ space. The local meteoric water line (LMWL) is derived using CNIP stations; station points are shown with closed grey circles. The local evaporation line (LEL) shows the isotopic composition of lake water (δ_L, n=3 years) samples collected in this study, illustrated with open circles. Throughflow systems occur at the most negative end of this line; evaporative systems are found at the most positive extent. The limiting isotopic composition ($\delta*$) calculated in the isotope mass-balance model is given (open, downward triangles) in the top right-hand corner of the graph. The isotopes in precipitation (open squares) are derived from yearly averaged data based on Bowen and Revenaugh (2003). The isotope mass-balance model calculates the δ_A component of the data set, and values are shown with open, upward triangles. An arrow points to the intercept between atmospheric isotope compositions, δ_A and the intercept of the δ_L data regression with the CNIP regression line. Not all systems fall directly along this line (see Gibson *et al.* 2002). The δ_E range is given by the dashed line, which is the extension of the linear trend through the isotopes in lake water, δ_L. The dotted line depicts results from Gibson *et al.* (2002), illustrating the range of isotope signals from 96 lakes located in the same regional area as this study.

VI. Conclusions

The water budget of the 50 lakes in the Boreal Forest was successfully modelled using a stable, water-isotope mass-balance approach. The results, shown in Fig. 1.23, indicate that the lake systems as modelled adhere well to the expected distribution of evaporated waters along the LEL and offset from the MWL in $\delta^{18}O$-$\delta^{2}H$ space. The isotopic range of lake waters also closely resembles an earlier study in this region (Gibson *et al.* 2002), shown by the dotted line in Fig. 1.23. The slope of the LEL for lake water isotopic signatures for the three years of the study are similar (Fig. 1.5), suggesting that the isotopic tracers do not vary to a large degree year-to-year, and that the three year average signal is indicative of long-term hydrologic status of the lake systems under consideration.

The isotopic results also indicate that there is naturally a wide-range in hydrologic conditions across the study region. This is reflective of the range of lake drainage patterns, lake and catchment morphologies, and soils and vegetation characteristics, as observed across the study sites during field experiments and via data exploration (see Chapter 2 for further discussion). The hydrologic variation observed in landscape features was also reflected within the isotopic results. Additionally, each yearly (2002 – 2004) derivation for isotope lake water signatures had a consistent slope value (LEL). These indications suggest that this analysis is based on repeatable information reflective of the hydrologic status of the catchments. Therefore, this information can be used to estimate water balance factors to compare similar and divergent lake systems, and to employ supplementary assessments such as water-yield estimates. The approach enables spatially distinct analysis of hydrologic characteristics across a regional study zone with relative ease of implementation into routine water monitoring schedules.

Climate variables input for the isotope model including precipitation, evaporation, temperature and relative humidity, are similar to those values published in other studies. Precipitation and evaporation values fall into ranges similar to those published by Strong and Leggat (1992), Abraham (1999) and the Hydrologic Atlas of Canada (denHartog and Ferguson 1978). The three years of study were also examined to ensure that one single, exceptional year was not affecting the isotope mass-balance model output results. Comparative analysis was undertaken using the long-term climatology and the annual minimum, maximum and averages and the monthly averages for temperature and annual and monthly averages for rain, snow and precipitation at the Fort McMurray climate station. The variation found in the year-to-year temperature and precipitation based on analysis at the Fort McMurray climate station was different from the long-term mean for 2004 temperatures and for snowfall during 2002. Despite these differences, the effects are not anticipated to alter isotope mass-balance model output greatly because of the use of temporal data averaging (isotopes in lake water) and sampling protocol maintained throughout the study. The most sensitive climate parameter (relative humidity), on the other hand, could not be analysed because of a lack of data.

Gridded climate model data was used to estimate climate variables. While there is an inherent difference in scale between the gridded data and the scale of the catchments under study, this information was necessary to use to derive model results for the regional area. For this reason, a detailed comparison and evaluation of each climate variable was undertaken to select the best data set for use in this region. In the future, this research would benefit from corroboration with finer-scale information to determine a benchmark data set and to work towards improvements in the scalar accuracy of the climate data as applied in this study.

Testing of the data model included analysis of the appropriate model approach, testing of input climate data variables, and examining flux-weighting results. Three model scenarios were examined; the dual fit application constrained equilibrium processes and therefore was selected as the best model approach for use in the final isotope mass-balance model. To test climate variables, comparative climate data sets were downloaded and examined to determine the most appropriate data to apply in this region. Testing of the climate data was challenging, because many of the variables simply had no known value (i.e., no long-term climate station data were available for individual lake sites), making comparison of these data with established baselines impossible. Therefore, a base case data set was used to determine which variants of climate input data (such as ECMWF or CRU data sets) deviated from the base case. This analysis determined that temperature and evaporation data sets are not sensitive to fluctuations observed in most climate data sets, while relative humidity was observed to be more sensitive than both temperature and evaporation. While variations in precipitation input values generated significantly different outputs compared to base case model, this variation occurred primarily because of the amount-weighting procedure applied in the test model framework. Therefore, this approach was not used in the final isotope mass-balance model. Model output (E/I) variations of up to 15% were found for reasonable approximations of climate input data. Evaporation flux weighting was also examined to determine the impact of this process on model input data. Results were similar to model input/output testing in that relative humidity was found to be a sensitive variable.

Sensitivity analysis was performed by holding isotope mass-balance model variables constant while examining the percentage difference in E/I as a result of altering one factor (for example, relative humidity) and observing the change across a limited set of expected isotopic conditions (Gibson *et al.* 1993a). The results of this analysis indicate that at the throughflow scale, isotopes in precipitation are sensitive on the order of 30% and at the evaporative scale, relative humidity is sensitive on the order of 25%. Isotopes in precipitation are sensitive and therefore smoothed, GNIP estimates (Bowen and Revenaugh 2003) should be verified through collection of point samples of precipitation, as undertaken in this study. Relative humidity, on the other hand, was not verified during this study. Future research work should consider validating relative humidity estimates using field-based monitoring at lake sites.

Hydrologic conditions (E/I) found at study sites ranged from highly throughflow systems with high water-yields in the Birch and Caribou Mountains, to more evaporative systems with lower water-yields located in West Fort McMurray and in the Stony Mountains. A high level of variability was found between the lake systems in this regional study; which complicated the hydrologic picture in terms of categorizing catchments into meaningful classes for modelling. In this study, many of the geo-environmental parameters were strongly correlated (see Chapter 2); however, the overall indication was that larger, deeper lake systems with steeper slopes and higher water-yields were generally located in the more northern and/or mountainous study regions. Throughflow systems occur likely as a result of geological parameters occurring in these higher latitude study regions, such as larger lake surface areas, lower drainage ratios (Fig. 1.21), and steeper slopes (Table 1.9). Evaporation also tends to be lower in the more northerly sites; therefore, the possibility that more catchment water could be available for runoff should also be considered as a contributing factor to higher water-yield. Slope is a strong indicator of hydrology within lake systems (Rasmussen *et al.* 1989): higher slopes could indicate greater percentages of uplands within the catchments, which could be an indication of water-yield and hydrologic status of a watershed.

Implications for Modelling Analysis

Examination of hydrologic parameters across a regional data set using an isotopic mass-balance model has established a baseline for hydrologic range and variation present within sites occurring primarily in the Boreal Plains ecozone of northeastern Alberta. This research supports earlier work (Gibson *et al.* 2002, Prepas *et al.* 2001) completed in the region, but extends modelling and sensitivity analysis as proposed in those papers to determine threshold values and sensitive variables within the isotope mass-balance model structure and in terms of model outputs. This allows for a clear understanding of the allowable range of variation in terms of input parameters and variables found both in nature and within gridded and GCM data sets. This also aids understanding of the impact of those variations within the isotope mass-balance model framework. This testing approach provided insight into both the isotope mass-balance model reactions and model robustness, and will be valuable for scientists attempting to apply similar hydrologic models in the Boreal Plains.

This research study supports conclusions of earlier workers (Gibson *et al.* 1993a) that found some variables, such as relative humidity, to be more sensitive. This is valuable information, as relative humidity is one of the more commonly difficult variables to define; for this reason, understanding its importance in the model framework is essential to accurate definition of hydrologic parameters. Future research should continue to examine the influence of flux-weighting parameters, and consider applying a daily flux-weighting application to compare to the monthly process used in this research. Currently, other workers are undertaking directed study at select lake sites (NE7 and SM8). This program will capture detailed information at hydrologic nodes across the study catchments and collect isotopic signatures from select hydrologic landscape units (HLUs), such as wetlands and upland landscape features. Thus, the concepts and baseline understanding of Boreal Plain hydrology as outlined in this chapter will be continue to be developed.

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Chapter 2 : Regional hydrologic, physical and chemical interactions of Boreal Plains lakes systems, NE Alberta, Canada

Abstract

A study was conducted to examine relationships between hydrology, physical properties and lake chemistry and improve assessment of the susceptibility of these aquatic freshwater ecosystems to acid emissions from projected oil sands operations in the area. A detailed analysis of 40 catchments applied the use of an isotope mass-balance model to characterize catchment hydrology and a GIS to derive edaphic factors generally governing acid relations, including; geology, soils, landscape cover type, and drainage ratios. Results indicate that base cation concentrations and associated acidic buffering capacities were highest in lowlands that had strong groundwater inputs as a result of wetlands coverage, and in particular, fens. Lakes in the Birch Mountains received groundwater inflow from connections with deep, regional aquifer systems, which provided buffering input from acidic contributions from the high percentage of bogs coverage in these catchments. Lakes located in NE Fort McMurray appear to be acid-sensitive owing to their sandy soils and high flushing rates, but overall close connection between wetlands and groundwater sources may buffer acidic contributions in lakes of this region. West Fort McMurray lakes appear buffered but may also be experiencing high inputs of strong organic acids in their basins owing to similarly high wetland coverage. Sensitive systems in the Stony Mountains occur where lakes have low buffering capacity and greater than 65% wetland cover. Long water residence times and low water-yields could also be affecting acid levels at these sites. These findings improve on existing estimates that used the water survey gauging stations to measure runoff and thereby achieve a scale consistent with the analysis of water chemistry and critical acid loadings applications for headwater basins.

I. Introduction

Forested watersheds in the western Boreal Plain are subject to potential impacts as a result of various industrial activities, including the extraction and processing of oil sands in northeastern Alberta's Athabasca region (AEP 1998). These broad-scale disturbances, in conjunction with other environmental stressors, are raising concern regarding water quantity and quality in the Boreal Forest (Putz *et al.* 2003), and have led to the development of new management frameworks (CEMA 2004, Chanasyk *et al.* 2003) whose purpose is to monitor acid deposition to, and its effects on, aquatic ecosystems. A need exists for baseline studies that characterize hydrologic water balance in the northern Boreal Plain (Buttle *et al.* 2005, Carignan and Steedman 2000), as well as for innovative research regarding oil sands development and the potential impacts of related emissions (Shell 2005) on surface waters in this region. Several studies have integrated changes in catchment hydrology and biogeochemistry from extensive tree removal by forestry (Allen *et al.* 2003, Gibson *et al.* 2002, Halsey *et al.* 1997, Prepas *et al.* 2003, Prepas *et al.* 2001). Presently, no studies have investigated these relations in a similar fashion for recent oil sands developments and estimates for projected expansions in Alberta's Athabasca regional area (see Shell 2005). While many similarities in the edaphic factors considered in other studies exist for the oil sands region, the impacts are also quite different. Impacts are chronic, influencing hydrology through large-scale drawdown in aquifers and disturbance of surficial hydrology, and widespread deposition of chemical constituents (e.g. nitrogen, sulphate, metals, etc.) from industrial activity.

In Chapter 1, a need was identified to improve estimates of water balance in remote regions of the Boreal Plains, where little or no hydrologic data existed. A method using an isotopic-mass-balance model was improved to address the requirement. The approach applied was ideal because it had few constraints common to alternate water balance estimates (LaBaugh 1986, NWWG 1998, Winter 1981). This chapter focuses on the next step in this assessment by linking hydrology to landscape features and lake water chemistry and within this context, examining the interactions between biogeochemistry as reflected in the landscape and vegetation. For this study, annual hydrologic water balance indicators, including throughflow status, flushing rates and water-yields were used to gain insight on relationships occurring at 40 lake sites. In addition, landscape features such as percent and type of forest cover and peatland type and coverage were summarized for each study catchment. The work aims to derive relationships between hydrology and lake water chemistry to develop an understanding of physical features as proxies for edaphic biogeochemical processes for this peatland dominated region.

Developing the initial, empirically-based understanding will develop the foundation for planned testing of process-based interactions and the construction of distributed models, thus leading the way for consideration of potential impacts across a range of topographic and landscape conditions found within Boreal Plains upland and lowland systems.

This chapter will focus on presenting the results of Chapter 1 along with landscape and chemical interactions analysed at lake systems in the Boreal Plains region of Canada. Although much is still unknown about the hydrology in this region, this chapter attempts to bring together the results of isotopic mass-balance assessment with landscape and chemistry analysis to focus attention on the processes at hand in determining acidic relations in this region. Following this the theoretical basis for this research are briefly presented. For further explanation of the isotope mass-balance model and approach, please see Chapter 1. Study site characteristics are described, and a detailed discussion of the year-to-year variability found within the three years of the study is presented. Methods are outlined for statistical analysis, although detailed methodology is outlined in Chapter 1 pertaining to field sampling, and physical and climate data collection and processing. Results and discussion represent the main body of work in this chapter. Lake water balance is presented and discussed in the context of recent research on the Boreal Plain. Major processes dominating hydrology relations at these sites are presented. Lake water chemistry interactions are provided, with details on conductivity, major ion chemistry, pH, DOC, TN and TP. A summary of the major findings documented in this chapter concludes this work.

II. Theory

The annual water balance of the 50 acid-sensitive lakes that form the basis for this study was calculated using an isotope mass-balance model. The theoretical model is described in detail in Chapter 1 of this thesis. Overall, the key hydrologic indicators, based on the isotope hydrology are: the evaporation/inflow ratio, water residence time, and water-yield (Wy, m^3), which may also be expressed as a depth equivalent (mm) or runoff ratio (mm/mm precipitation) by dividing by the net catchment area if watershed area can be accurately estimated. These factors provide perspective on the lake water budget, i.e., the partitioning of water losses by evaporation versus non-evaporation (liquid surface and subsurface outflow); residence time, which is the appropriate time-scale for establishing the temporal footprint of the chemical signatures; and water-yield, which is useful for investigating linkages between the lake and the landscape.

III. Site Description

The research area is situated in northeastern Alberta, Canada (Fig. 2.1, Table 2.1). The lakes under study are located in the upland regions of the preglacial remnant Birch Mountains, in the more southerly Stony Mountains and in the lowland regions of NE and West Fort McMurray. All forty lakes are proximal to the town of Fort McMurray (56° 39" N, 111° 13" W) and its oil sands operations, and are associated with the Boreal Plain Mixedwood (NE Fort McMurray, Stony Mountains and West Fort McMurray) and Northlands ecoregions (Birch Mountains). Fig. 2.1 shows the potential acidifying isopleths (Shell 2005), illustrating that lake sites within NE and West Fort McMurray and the Stony Mountains fall within the 0.25 and 0.17 Keq/ha/yr range of emission of SO_2 and NOx.

Bedrock and surficial geology in the study catchments consist of several major formations and materials (AGS 2004, Abboud *et al.* 2002). The upland systems overlie bedrock composed primarily of marine and deltaic shales and siltstones (Halsey *et al.* 1997), that are known to be easily erodable and have high salt contents. Lowland lake systems primarily reside on fine-grained quartzose and feldspathic sandstone bedrock of non-marine origin (Birch Mountains). Most lowland, surficial catchment materials are comprised of organics, with stratified drift formations of varying thickness. Upland sites are generally comprised of silty, sandy mineral composites. Fine-grained silts and clays, intermixed with glaciolacustrine sediments occur at lakes NE9, NE10 and WF4. Eolian materials of reworked fluvio-lacustrine sands are present in the Stony Mountains, NE and West Fort McMurray (see for example WF5, WF6, WF7 and WF8; Andriashek 2005); these deposits often occur in conjunction with moderate to fine morainal tills, combined with varying amounts of coarse sands, silts and gravel (NE6, NE7) in headwater zones of these drainages. The Birch Mountains are composed primarily of morainal deposits, with fine-loamy to clayey materials and some glaciofluvial and eolian deposits (Turchenek and Lindsay 1982). These features can provide rapid drainage and high storage capacity (Hendry 1982).

Soils in the Stony Mountains and in NE and West Fort McMurray are comprised of organics, luvisols, and brunisols. The Birch Mountains contain primarily cryosolic and brunisolic soils (SLCWG 2004, Strong and Leggat 1992). Organic peatlands comprise the majority of cover types, and catchments are comprised of varying amounts of bogs, fens and mineral uplands (Vitt *et al.* 1996, Table 2.1). In NE Fort McMurray, bogs and fens comprise approximately 20% and 63% of catchments, respectively, while West Fort McMurray systems contain less bog (9%) but are similarly dominated by fens (62%) (Abboud *et al.* 2002). The Birch and Stony Mountains consist primarily of bog systems, with lesser amounts of fen (ASRD 2001, Vitt *et al.* 1996).

Upland catchment areas contain variable forest cover: *Picea mariana* is the dominant cover type, comprising 51% of the catchments analysed (n = 24), with *Populus tremuloides* (9%), *Pinus banksiana* (9%) and *Larix laricina* (5%) as second, third and fourth most common, respectively. The Stony and the Birch uplands contain mostly coniferous forests (*Picea mariana* and *Pinus banksiana*), with minor amounts of *Populus tremuloides* and *Larix laricina*. NE Fort McMurray watersheds contain approximately 15% *Larix laricina* and 8% *Populus tremuloides*, and have an overall conifer coverage twofold greater than West Fort McMurray; the latter has the greatest amount of *Populus tremuloides* in its headwaters, and has nearly equal amounts of conifer and decidous cover. Fire disturbances are very common in the Boreal region (McEachern *et al.* 2000): almost 55% of BM10's catchment was burned in 2001, and the landscape surrounding SM7 was disturbed by both fire and logging during the late 1990's.

Table 2.1 Physical properties for the study lakes. Lat = latitude, Long = longitude, Elev = elevation, Area = lake surface area, DBA = drainage basin area, Vol = lake volume, Slope = mean percentage catchment slope, τ = residence time, Upland = percentage upland found in catchment, Peat = percentage peatland found in the catchment.

Lake	*Lat (dd)*	*Long (dd)*	*Elev (masl)*	*Area (km^2)*	*DBA (km^2)*	*Vol (mm)*	*Slope (%)*	*τ (days)*	*Upland (%)*	*Peat (%)*
Low/Mod Water-yield										
NE2	57.09	-110.75	600	0.34	17.32	1271	1.5	120	35%	65%
NE5	56.89	-110.90	488	1.89	21.47	914	0.6	142	18%	77%
NE6	57.27	-110.90	574	0.37	11.06	879	1.8	115	38%	62%
NE8	57.23	-110.75	579	0.11	6.59	804	1.0	173	6%	94%
NE9	56.77	-110.91	483	3.15	23.25	1115	0.6	122	34%	66%
NE10	56.64	-110.20	484	4.19	31.86	771	1.1	84	54%	45%
SM2	55.79	-111.83	671	1.97	26.27	571	1.1	105	43%	57%
SM4	56.15	-111.23	726	0.53	12.52	706	1.8	157	15%	85%
SM5	56.17	-111.55	720	1.06	7.35	1149	2.2	92	50%	50%

Lake	*Lat (dd)*	*Long (dd)*	*Elev (masl)*	*Area (km^2)*	*DBA (km^2)*	*Vol (mm)*	*Slope (%)*	*τ (days)*	*Upland (%)*	*Peat (%)*
SM7	55.68	-111.83	670	1.48	7.26	1277	2.6	17	91%	9%
WF1	56.35	-113.18	614	3.20	27.42	585	0.6	127	32%	68%
WF2	56.24	-113.14	630	0.76	24.13	938	0.7	74	60%	40%
WF3	55.91	-112.86	563	2.16	40.31	966	1.0	157	15%	85%
WF4	57.15	-111.98	360	0.03	1.82	837	1.5	127	31%	69%
WF5	56.80	-111.92	510	0.23	7.12	754	1.5	121	35%	65%
WF6	56.81	-111.72	498	0.18	5.30	974	1.6	106	43%	57%
WF8	56.77	-111.95	512	2.02	29.10	720	0.5	144	22%	78%
WF7	56.78	-111.79	516	0.08	1.80	794	3.4	44	76%	24%
BM3	57.65	-112.62	684	0.97	29.59	1381	5.4	21	89%	11%
BM10	57.31	-112.40	590	0.39	5.49	370	1.4	110	40%	60%
BM11	57.69	-111.91	787	0.06	1.53	238	3.3	12	94%	6%
Avg			**590**	**1.2**	**16.2**	**850**	**1.7**	**105**	**43%**	**57%**
High Water-yield										
NE1	57.15	110.85	592	0.65	13.76	1200	0.8	149	19%	81%
NE3	57.05	110.59	654	0.58	7.22	1448	1.4	114	36%	62%
NE4	57.96	110.40	356	1.16	17.14	614	1.8	143	23%	77%
NE7	57.15	110.86	592	0.11	4.19	1004	1.3	118	36%	64%
NE11	57.29	111.24	328	5.75	74.67	1324	1.7	57	68%	31%
SM1	55.76	110.76	571	2.37	9.46	673	1.3	36	81%	19%
SM9	56.22	111.25	721	1.07	10.54	577	1.1	140	24%	76%
SM8	56.21	111.20	722	1.91	11.63	886	1.0	96	48%	52%
SM3	56.20	111.37	721	1.86	9.54	1446	2.2	65	65%	35%
SM6	56.22	111.17	721	0.70	4.09	884	2.0	76	59%	41%
BM1	57.41	112.93	789	17.03	68.35	5820	2.5	34	82%	18%
BM2	57.42	112.69	724	43.97	163.62	10509	3.6	22	88%	12%
BM4	57.69	112.74	662	4.26	38.36	429	2.9	40	78%	22%
BM5	57.76	112.58	678	2.64	30.53	457	4.2	18	90%	10%
BM6	57.85	112.97	724	1.29	19.69	496	1.6	65	62%	35%
BM7	58.06	112.27	757	0.68	8.49	659	1.4	78	55%	42%
BM8	57.77	112.40	661	1.22	33.90	1118	4.3	43	77%	23%
BM9	57.70	112.38	747	3.48	33.75	3199	1.8	73	60%	40%
Avg			**651**	**5.0**	**31.1**	**1819**	**2.0**	**76**	**58%**	**41%**

Thirty-year (1971–2000) air temperature normals at Fort McMurray range from 16.8° C in summer (July) and –18.8° C in winter (January) (MSC 2004). The open-water season is initiated in May, when winter thaw recharges lakes with melt waters, and active hydrologic exchange begins across the landscape. Freeze-up begins in October and lakes are usually ice-covered by November, at which time evaporation processes and precipitation in the form of rainfall cease. Mean annual precipitation is 456 mm, 74% of which falls as rain during the open-water season, with the remainder falling as snow during winter months (MSC 2004). Peak runoff occurs in conjunction with snowmelt; however, secondary peaks can occur in late-August because of high rainfall (Winter and Woo 1990, Fig. 2.2). Average annual evaporation is 480 mm (Hamon 1961, New *et al.* 1999), and January relative humidity is 75%, while in July it is 70% (New *et al.* 2002).

Climate conditions in this region assist with permafrost development in some regions. Soil freezing may also occur within some catchments. Permafrost features such as collapse scars and plateau bogs are most common in the Birch Mountain uplands (Halsey *et al.* 1997), while permafrost generally occurs in the remainder of the sites as isolated patches (Brown 1998).

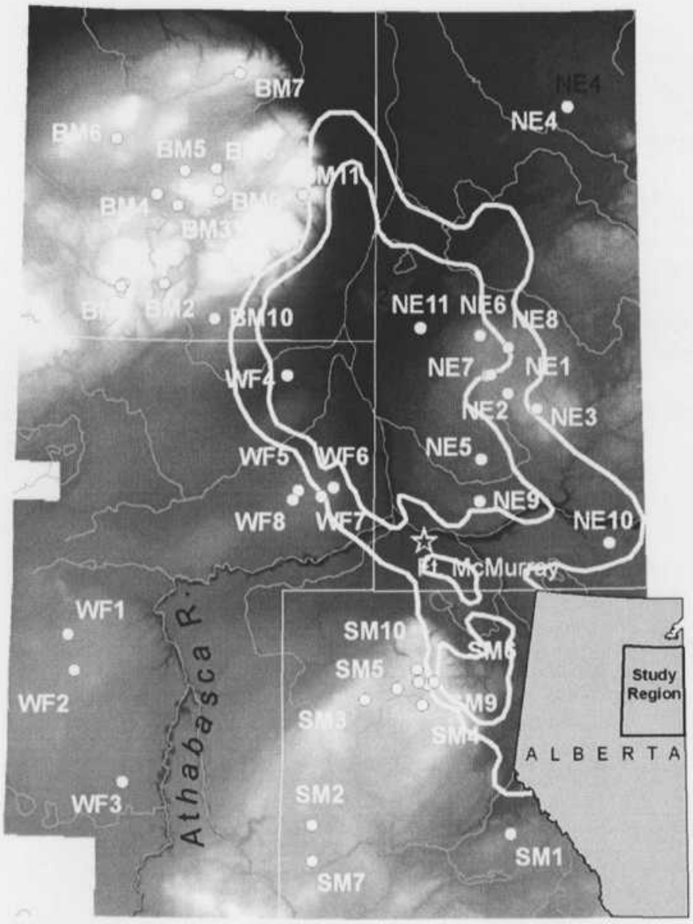

Figure 2.1 Map of study lakes and location of study area in Alberta. Potential acidifying input isopleths are shown for the regional area, indicating the location of the 0.25 (inner line) and the 0.17 (outer line) Keq/ha/yr range based on the most recent environmental impact assessment (EIA, Shell 2005). These isopleth lines indicate projected emissions of SOx and NOx for the regional area. The lakes sites are shown with their associated identification codes (SM5, for example), which also indicate the regional area. NE = Northeast Fort McMurray, SM = Stony Mountains, WF = West Fort McMurray and BM = Birch Mountains. The inset shows the project location in northeastern Alberta.

Analysis of data from the Fort McMurray climate station (see Chapter 1 for methodology) indicates that the three years of study were different from the long-term mean (Table 1.5, 1.6 of Chapter 1, and Table 2.2 below). In general, temperature and precipitation data show: 2001 might have been slightly warmer and drier than the long-term average; 2002 was cooler and slightly drier than the long-term average; 2003 was warmer and wetter; and 2004 was the coolest and driest year of the study period as compared to the long-term average. Significant differences were found between 2004 temperature versus the long-term average temperature and average monthly snowfall in 2002 versus the long-term average monthly snowfall.

Table 2.2 The open-water monthly temperature and precipitation for pre-season (2001) and the years of study as compared to the long-term mean (1971-2000). Data were obtained from the MSC (2004) climate records for the Fort McMurray station.

	May	*Jun*	*Jul*	*Aug*	*Sep*	*Oct*
Temperature (°C)						
2001	10.4	14.3	17.6	16.7	11.6	1.0
2002	6.7	15.6	16.8	14.3	9.0	-2.4
2003	9.3	14.0	17.6	16.1	9.5	4.4
2004	5.7	13.3	18	12.7	7.9	1.1
Long-term	10.4	14.7	16.8	15.3	9.4	2.8
Precipitation (mm)						
2001	50.4	50.6	56	50.3	26.5	19.8
2002	19.6	58.8	145.9	57.8	36.0	29.6
2003	52.4	84.5	69.9	48.7	89.4	56.5
2004	54.6	16.0	36.5	17.0	56.0	12.0
Long-term	36.9	74.8	81.3	72.7	46.8	29.6

Examinations of six river gauging stations (07CB002, 07CD004, 07DA006, 07DA008, 07DB001, 07DC001, WSC 2004) from the regional area also provided an indication of the variability present within the three study years and the pre-study season (2001) (Fig. 2.2 presents a representative example). As the gauge is currently operated seasonally, data is not available into October for the 2001-2004 study years.

At the Muskeg River station (07DA008, Fig. 2.2), bimodal hydrograph peaks are present in the long-term average runoff. The 2001 pre-season had a slightly later freshet and higher flows through the spring season, and a late-summer runoff peak was not experienced at this site. Perhaps owing to the dry pre-season year, the entry year for this study (2002) was different from other years and the long-term average hydrograph for this site, and at all other stations examined. The seasonal freshet peak did not occur, and therefore the highest summer runoff occurred during mid-August. 2003 experienced seasonal freshet concurrent with the long-term average, which extended further into the summer season and then declined rapidly in August. Precipitation occurring late in fall of that year (September, Table 2.2) was observed as an increase in runoff from the catchment into October, however the cessation of monitoring during this time does not allow for further observation of this trend into the winter period. A warm spring in 2004 led to rapid melting of the snow pack and discharge over frozen soils in the spring (as observed at study sites), leaving little water for base flow contributions through the summer. Thus the river level sharply declined to a value either below the gauging datum or to an extremely minimal flow not-detectable by the runoff gauge. A small increase in the late summer season was observed. The hatched box in Fig. 2.2 shows the sampling period range for collection of water chemistry and isotope data for the three study years (late August to early September, depending on field conditions).

Given the information provided in the analysis of temperature and precipitation (see Chapter 1 for more details), and from the examination of the runoff records at stations throughout the regional study area, it appeared that 2003 was the most 'normal' year for which data was available. Therefore, it was reasonable to select the 2003 study year for the examining relationships between hydrology, physical landscape and lake water chemistry.

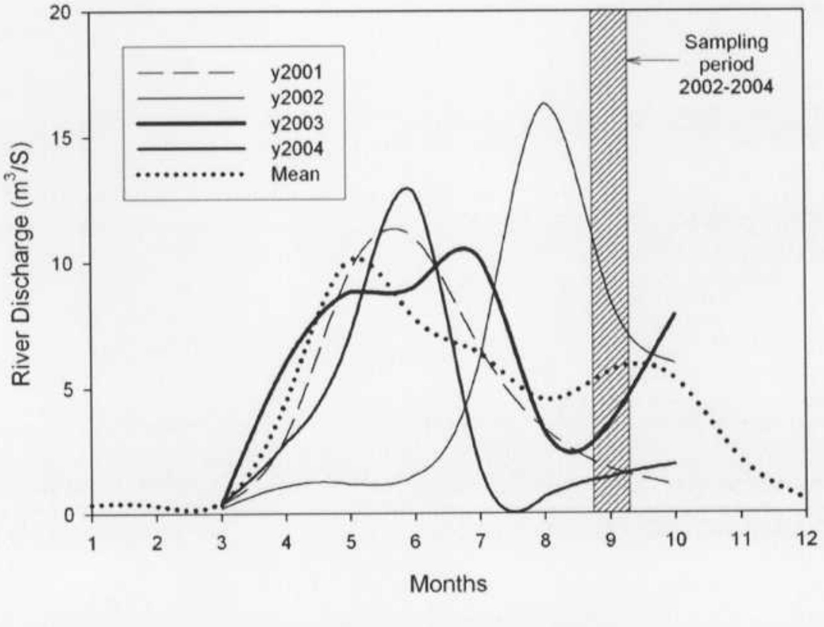

Figure 2.2 River discharge data from the Muskeg River Water Survey of Canada gauging station (07DA008). The mean annual runoff for all years (1974 to 2004) is presented with a thin, dotted line. The2001 pre-season is illustrated by a dashed line, the 2002-2004 study years are all solid lines, with the 2003 'normal' year given by the thickest line, followed by the 2004 season and finally the 2002 data is shown with a thin, solid line. See text above for further discussion.

IV. Methods

Lake water chemistry and isotopic samples were collected in the late summer/ early fall seasons of 2002, 2003 and 2004. A monthly open-water sampling program initiated in 2004 at ten lake sites supplemented the annual monitoring routine. Sample data collection, climate and physical data analysis is described in Chapter 1. Chemistry data were analysed at the University of Alberta according to the methods outlined in McEachern *et al.* (2000).

The method used for determining vegetation type varied, depending on the data set. Alberta Vegetation Inventory (AVI) data were classed into forest type both by individual species type and as a collapsed category of deciduous or conifer. AVI was used to classify bog and fen vegetation feature classes based on species composition, moisture regime height class, density (crown closure) and shrub type (ASRD 2001). The classification of soil types into bog, fen and till from Abboud *et al.* (2002) provided a basis for the compilation of bog and fen soil categories. Because previous studies in the area suggest that differences in the peat chemistry are minor (Halsey *et al.* 1997), and further division of specific bog and fen classes (permafrost bog, etc.) was considered unnecessary. Twenty-four catchments contained AVI data, while 26 watersheds had AOSERP data; and 11 catchments contained information from both data sets.

Statistical analysis

To test relationships between physical and hydrologic parameters, land cover types and lake water chemistry, statistical analyses were performed using Minitab Release 13. Chemistry results are based on the 2003 data, which were considered the most 'normal' of the three years studied in terms of hydrologic runoff values and climate data obtained from rivers and climate stations in the region (MSC 2004, Fig. 2.2, Table 2.2). The five Shield and five Caribou Mountain lakes sites were removed to focus analysis on Boreal Plain systems ($n = 40$). Factors were tested for normality and kurtosis using the Kolmogorov-Smirnov test and were either lognormal ($\ln_2$) or $\ln_2+x$ transformed (Appendix C). An arcsine transformation was used to normalize percentage values, for instance, those of bog and fen classes that were calculated in relation to the catchment area. Some variables were removed from the analysis because they could not be normalized.

As an initial scoping exercise, and to allow for appropriate application of further statistical tests, Pearsons's correlation matrices were created to determine significant correlations ($P \leq 0.05$) and to detect intercorrelation between independent factors.

Results from the correlation tests suggested that further testing of the data set should be undertaken to determine the nature of the relationships between hydrologic parameters, peatlands and chemical variables. Accordingly, the data set was divided into low/moderate and high water-yields (0–99 mm and 100–400 mm, respectively), and the Mann-Whitney test applied in order to determine if the hydrologic division resulted in significantly different physical and chemical characteristics. Box and whisker plots were used to display significant results ($P \leq 0.05$). The box frame indicates the 25–75% population, and the whiskers indicate the 10 and 90 percentiles and outliers; median and means are also given (Fig. 2.3, 2.4). The data set was then divided into percentage peatland or upland (Vitt *et al.* 1996), as well as bog or fen (Abboud *et al.* 2002), in the catchment to determine what differences in the hydrologic and water chemistry data populations may be driven by the peatland occurrence. Correlation matrices were also used as the basis for exploration using regression analysis of water-yield. Significantly correlated factors were input into univariate and stepwise multilinear regression models and tested to obtain the best fit. Data was only available for testing in 25 catchments Results are given for each variable that obtained a successful match (adjusted r^2 > 50% to 95%) to a linear trend.

V. Results and Discussion

Physical and Geographic-Environmental Parameters

The lakes systems examined in this study exhibit a broad range within their hydrologic, physical, and chemical properties (Tables 2.1 and 2.3). The study watersheds are primarily headwater systems, but range from shallow, small ponds (WF4, 1m deep, < 0.5 km^2), to systems such as Namur Lake (BM2, 27 m deep, 44 km^2). The average lake surface area and depth is 2.9 km^2 and 1.1 m, respectively. Lake morphometry also varies greatly, with systems located on the uplands regions having distinctly different lake shorelines than systems located on the lowland. Average catchment areas for the entire data set are approximately 23 km^2, with minimum and maximum catchment areas of 1.5 km^2 (BM11) and 164 km^2 (BM2), respectively. Average elevations in the study regions range from lowland sites west and northeast of Fort McMurray (~500 m) to high elevation systems located in the Birch and Stony Mountains (~700 m). Lakes have an average elevation range of 46 m, although systems in the Birch Mountains have average elevation ranges greater than 100m, and systems in West Fort McMurray have mean elevation ranges of 18 m. Slopes are low in this landscape; average slope is 1.9% in study catchments but catchment slopes range from 0.5% in NE Fort McMurray to 5.4% in the Birch Mountains.

Water-yields and Drainage Basin Features

In general, lakes with high water-yields were significantly larger in surface area, drainage basin area and depth than those with low/moderate water-yields. Slopes were also related to water-yields overall in this data set ($r = 0.46$, $P < 0.01$), consistent with increased water-yields from steeper sloped catchments elsewhere (Rasmussen *et al.* 1989). Stepwise, multilinear regression analysis indicated that net catchment area to lake volume (NCA/LVOL) and slope were accounting for 67% of the variation found in water-yield ($P < 0.01$). However, the net catchment area to lake volume ratio was greater in the low yield data population (30) than in the high water-yield lakes (14); low water-yield lake populations also had twofold drainage ratios of the high water-yield lake systems (12 vs. 23). The distinction is that the low water-yield systems were dominated by the catchment area in relation to lake water volume and surface area, while the high water-yield systems were not. Regression testing supported this, as the most important factors at high water-yield sites tested were lake depth, surface area and perimeter ($r^2 =$ 55%, $P < 0.01$).

Low water-yield systems had 15% more peatland versus upland within their catchments (57% vs. 43%, Table 2.1), which suggested that the hydrologic status of the catchment was related to the percentage of wetland in the catchment (Prepas *et al.* 2001). Fens were found to be the dominant cover type in the low water-yielding systems of NE and West Fort McMurray; and bogs tended to be associated with the high water-yield systems ($P < 0.05$). While fens typically produce more water-yield than bogs (Halsey *et al.* 1997), the observations in this study are consistent with similar lowland/upland comparisons in Alberta (McEachern et al. 2005). These workers found resistance to water movement (debris piles, beaver dens) and low gravitational forces for lateral flow maintained a greater proportion of wetlands, and in particular, fens.

Catchments throughout the region tend to contain clayey substrates in their lower draws, with eolian or sandy/silt till matrices comprising headwater catchment zones (Fenton 1984). Because of the prevalence of peatlands (primarily fens) at lowland sites (NE and West Fort McMurray), these saturated areas could be maintaining greater connections with their catchment storage zones, allowing for consistent translation of water and constituents from both the wetlands itself, and from storage in soils. Upland sites, on the other hand, where bogs are more common, are likely disconnected for a large percentage of the summer months, and only become contributing areas during times of high storm flow in the catchments, as found to be occurring in other locations in the Boreal Plain (Devito et al. 2005b). However, upland sites also contain large, deep lake systems, especially in the Birch Mountain region. These large lakes may have strong connections to groundwater inputs from regional aquifers. At the upland sites, therefore, lake depth becomes an important indicator of the lake hydrologic regime, as groundwater inflows tend to increase the amount of freshwater input to a lake system. While, lowland sites, cover types, such as wetland percentage (which in turn affects input of groundwater) or forest type, are the key drivers of hydrologic function.

Low water-yielding catchments also have greater amounts of deciduous species (such as *Populus tremuloides* and *Larix laricina*) occurring within their headwater slopes, and this relationship was significant ($U = 338$, $P = 0.02$; 15% compared with 5% in upland catchments). It is possible that these deciduous forest covers are using more water resources, thereby contributing to low water-yield in the catchment systems, especially if they are removing water stores from the catchment during dry years (Devito *et al.* 2005, Smerdon *et al.* 2005). Lowland forest covers, being more predominantly deciduous, will allow for maximum solar influx to ground cover, as leaf-out will not have occurred at the point of spring freshet.

Additionally, the late summer storm events common to this region occur during maximum evapotranspiration within the upper catchment zones of the fen-dominated/deciduous watersheds, which may result in water being evapotranspired that might otherwise be translated to the lake system. Sedge grasses, often the dominant cover type found in fens, are also effective evapotranspirers, as noted by Rouse *et al.* (2000). Mixing in the effective contributing area of drainage basins would obscure this ET signal in the downstream isotopic lake water composition (Hunt *et al.* 1996), and its impact would only be measured as a decline in water-yield. On the other hand, conifer forests found at uplands regions (35% and 30% for the BM and SM systems, respectively, vs. 27% in both NE and WF sites) may be contributing to greater snow drift capture and prolonged melt-out and release from residual snowbanks that may be partially shaded by evergreen *Picea mariana* and *Pinus banksiana*, dominant in the upland catchments of the Birch Mountains (Carey and Woo 2001).

Bogs located in the Birch Mountains may also be influenced to a degree by discontinuous permafrost and soil freezing. Sphagnum has been noted to have low thermal diffusity (Risebourough and Burn 1988); thus bogs may be more effective at retaining low temperatures further into spring freshet. This may cause greater runoff from frozen bog surfaces during snowmelt periods, especially if thermal regimes present within bog profiles prolong soil freeze and subsequently block water from infiltrating and in the till (Carey and Woo 1999). This process could be dominating the annual water balance at the upland locations.

Lakes located in the lowland, fen-dominated catchments have higher water temperatures, and permafrost is less common. These systems may are able to store large amounts of snowmelt waters in their highly conductive headwater tills at a key time of the hydrologic season. Fens are also associated with greater water table flux and drawn down in late summer (Lafleur 1990, Roulet 1991). Therefore, less water may be available for freezing during the over-winter period and development of frost lenses during spring freshet.

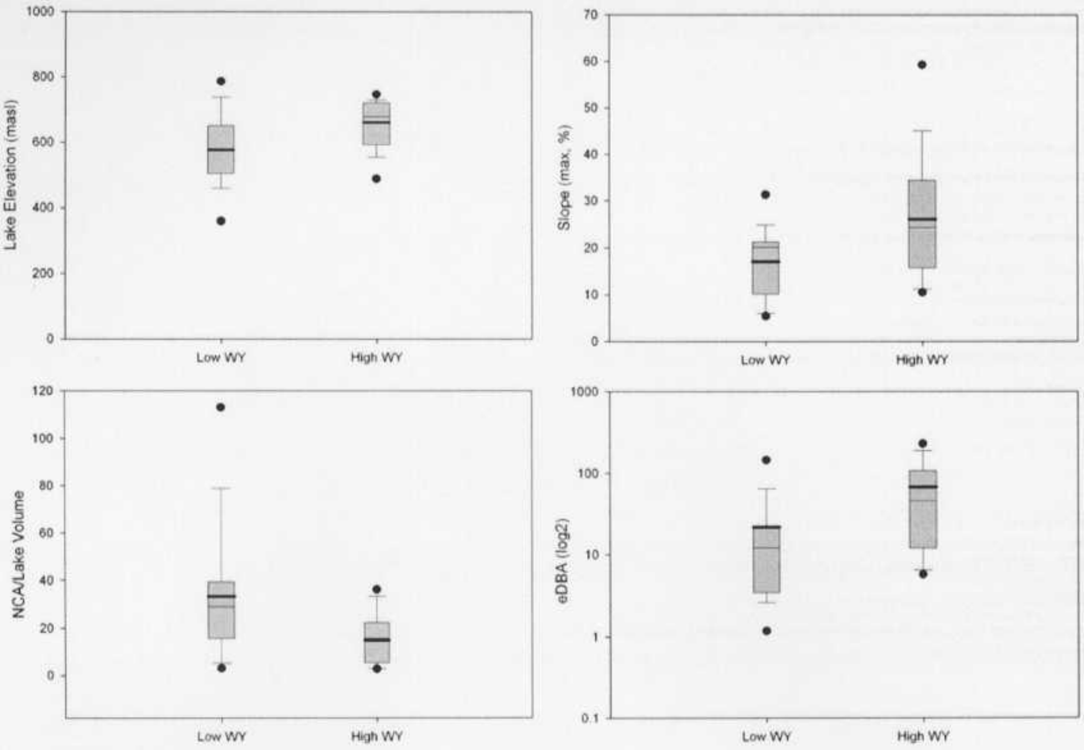

Figure 2.3 Box and whisker plots of significant parameters based on low and high water-yield divisions, showing lake elevation, slope, net catchment area/lake volume and eDBA. The box frame illustrates the 25–75% population, while whiskers show the 10 and 90 percentiles. Black circles indicate both high and low outliers. Horizontal lines inside boxes illustrate data set median (light) and mean (dark).

Physical and Hydrologic Relationships to Lake Water Chemistry

For almost all chemistry variables, high water-yield lake systems had significantly smaller mean values versus lower water-yield systems (examples are given in Fig. 2.4). Colour and TP are the exceptions: colour was very similar in both the high and low water-yield lakes, (157 mg/L Pt in the high water-yield lakes, versus 138 mg/L Pt in the low water-yield lakes), and total phosphorus did not differ between the two populations. Significant negative correlations were detected between water-yield and DOC, TN, conductivity, Ca, pH, alkalinity and bicarbonate (see results in Table 2.3). Relationships in the high water-yield data set were stronger for DOC, TN and colour.

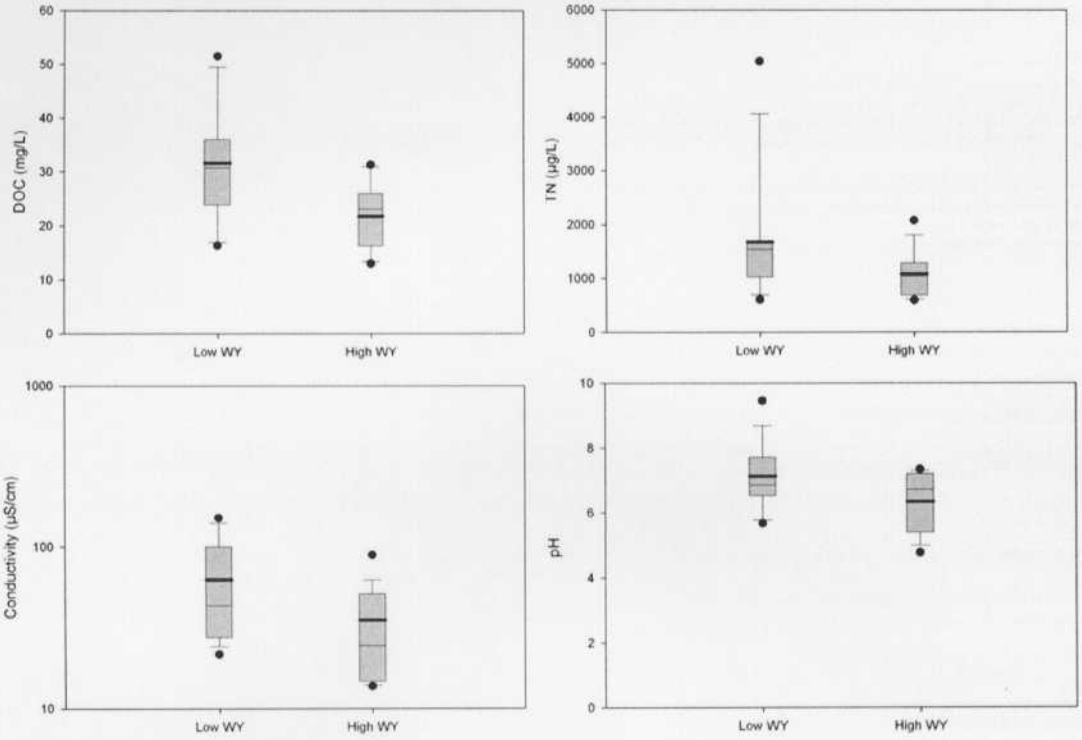

Figure 2.4 Box and whisker plots of significantly different chemistry variables by divisions of low and high water-yield. DOC, TN, Conductivity and pH are shown. The box frame illustrates the 25–75% population, while whiskers show the 10 and 90 percentiles. Black circles indicate high and low outliers. Horizontal lines inside boxes illustrate data set median (light) and mean (dark).

Conductivity and major ions were lower on average than those values observed in other Boreal Plain sites (Mitchell and Prepas 1990, Prepas *et al.* 2001), the Caribou Mountains (McEachern *et al.* 2000), Wood Buffalo National Park lakes (Moser *et al.* 1998) and lakes in the Swan Hills (Allen *et al.* 2003). Results as observed in this study are most similar to study sites examined by Halsey *et al.* (1997). The lowest values for conductivity and major ions are found on the Stony Mountains, while NE Fort and West McMurray exhibits the highest values, including DIC, Ca, Mg, Na, alkalinity, and bicarbonate.

Table 2.3 Lake chemistry by regional area. BM = Birch Mountains, NE = NE Fort McMurray, SM = Stony Mountains, WF = West Fort McMurray. Std dev = standard deviation. SE = Standard Error.

	Region	*Min*	*Max*	*Mean*	*Median*	*Std Dev*	*SE (Mean)*
Total Nitrogen (TN) (µg/L)	BM	307	3816	1214	834	1014	306
	NE	611	1639	1074	974	413	124
	SM	621	1714	1102	1104	309	98
	WF	1137	5040	1949	1575	1292	457
Total Phosphorus (TP) (µg/L)	BM	18.2	340.8	119.9	90.2	108.6	32.7
	NE	14.8	105	34.52	27.4	25.14	7.58
	SM	30.4	108.9	66.6	62.75	31.24	9.88
	WF	19.1	199	66.4	46.3	60.8	21.5
Dissolved Organic Carbon (DOC) (mg/L)	BM	8.02	48.96	22.08	23.1	11.66	3.52
	NE	13.45	31.37	25.36	26.42	6.31	1.9
	SM	12.97	28.73	19.71	19.16	4.8	1.52
	WF	20.62	51.51	35.31	34.93	10.58	3.74
Dissolved Inorganic Carbon (DIC) (mg/L)	BM	0.27	7.98	2.40	1.61	2.22	0.67
	NE	0.24	15.70	5.93	3.45	6.24	1.88
	SM	0.30	3.44	0.99	0.53	0.99	0.31
	WF	0.40	9.03	4.34	4.15	3.04	1.08
Sulphate (SO_4) (mg/L)	BM	0.27	9.97	3.96	3.95	3.21	0.97
	NE	0.00	3.09	0.67	0.44	0.84	0.25
	SM	0.27	13.87	2.09	0.74	4.16	1.31
	WF	0.27	9.07	1.82	0.82	2.97	1.05
Sodium (Na) (mg/L)	BM	0.83	8.55	2.54	2.45	2.25	0.68
	NE	0.46	8.41	2.57	2.09	2.59	0.78
	SM	0.62	1.42	0.91	0.78	0.29	0.09
	WF	0.68	6.17	1.98	1.09	1.86	0.66
Calcium (Ca) (mg/L)	BM	0.56	12	4.77	5.19	3.10	0.93
	NE	2.66	21.2	8.88	5.61	6.59	1.99
	SM	1.16	5.69	2.28	1.7	1.386	0.438
	WF	3.2	12.8	8.42	8.38	3.68	1.3
Magnesium (Mg) (mg/L)	BM	0.15	4.6	1.604	1.57	1.167	0.352
	NE	0.91	7.33	2.921	1.64	2.448	0.738
	SM	0.33	1.94	0.745	0.5	0.539	0.17
	WF	0.71	5.2	2.64	2.69	1.624	0.574
Alkalinity (ALK) (mg/L as $CaCO_3$)	BM	0	45.3	13.36	9.38	12.09	3.64
	NE	3.92	78.84	31.38	18.78	30.6	9.23
	SM	1.13	18.41	5.73	4.12	5.38	1.7
	WF	4.79	42.17	24.59	24.04	14.56	5.15
Conductivity (COND) (µS/cm)	BM	16.5	109.9	44.92	47.5	27.16	8.19
	NE	22.3	163.8	69.5	45.8	55.9	16.9
	SM	13.7	45	21.26	15.8	10.38	3.28
	WF	27.4	117.1	63.4	58.9	31.5	11.1
pH	BM	4.33	8.07	6.65	6.85	1.00	0.30
	NE	5.37	9.46	7.07	6.98	1.22	0.37
	SM	4.76	7.15	5.91	5.87	0.82	0.26
	WF	5.67	7.97	7.07	7.25	0.69	0.25
Colour (COL) (mg/L Pt)	BM	11	11.9	485.6	175.8	162.4	146.7
	NE	11	27.9	299.7	156.3	148.3	108.4
	SM	10	43.2	340.3	151	117	110.9
	WF	8	25.8	429.4	158.1	124.7	125.6
Chlorophyll-*a* (µg/L)	BM	11	2.6	128	35	15	43.3
	NE	11	2.54	31.64	12.37	9.72	10.15
	SM	10	7.33	21.93	13.88	14.07	4.44
	WF	8	1.5	92.5	20.6	6.9	30.2

Table 2.4. Pearson's correlation matrix for physical, hydrologic, land cover and chemical variables. Elev = elevation, eDBA = effective drainage basin area, NCA/Vol = net catchment area/lake volume, DR = drainage ratio, E/I = evaporation over inflow index, τ = residence time, Wy = water-yield, WET = wetland, Conf = percentage of catchment conifer forest cover, Decid = percentage of catchment deciduous forest cover, Bog = percentage of catchment bog cover, Fen = percentage of catchment fen cover. All transformations are as noted in Appendix C.

	Elev (masl)	*eDBA*	*NCA/ Vol*	*DR*	*E/I*$^+$	τ^+
Total Nitrogen (μg/L)	-0.42**	-0.45**	0.31	0.08	0.55**	-0.04
Total Phosphorus (μg/L)	0.29	-0.09	0.21	-0.05	0.23	-0.23
Dissolved Organic Carbon (mg/L)	-0.49**	-0.33*	0.64*	0.55**	0.12	-0.36*
Dissolved Inorganic Carbon (mg/L)	-0.53**	-0.03	0.02	-0.00	0.08	0.05
Calcium (mg/L)	-0.69**	-0.03	0.16	0.24	0.18	0.16
Magnesium (mg/L)	-0.36*	-0.23	-0.01	-0.09	0.28	0.11
Sodium (Na, mg/L)	-0.53**	0.10	0.07	0.05	0.08	0.01
Potassium (K, mg/L)	-0.18	-0.29*	-0.21	-0.25	0.61**	0.50**
Sulfate (SO_4, mg/L)	-0.11	0.19	0.17	0.21	-0.16	-0.12
Alkalinity (mg/L as $CaCO_3$)	-0.65**	-0.08	0.04	0.09	0.27	0.25
Bicarbonate (mg/L)	-0.64**	-0.08	0.05	0.10	0.26	0.25
Conductivity (μS/cm)	-0.67**	-0.04	0.09	0.12	0.26	0.21
pH	-0.55**	-0.11	-0.07	-0.02	0.37*	0.36*
Colour (mg/L Pt)	0.07	0.10	0.60**	0.56**	-0.46**	-0.70**
Chlorophyll-a (μg/L)	0.07	-0.12	0.10	-0.07	0.24	-0.09

	Wy (mm)	WET (%)$^+$	Conif (%)	Decid (%)$^+$	Bog (%)$^+$	Fen (%)$^+$
Total Nitrogen (μg/L)	-0.62**	0.16	-0.69**	0.18	0.03	0.07
Total Phosphorus (μg/L)	-0.17	-0.18	-0.42*	-0.43*	0.50**	-0.37
Dissolved Organic Carbon (mg/L)	-0.60**	0.40*	-0.61**	0.52**	-0.16	0.31
Dissolved Inorganic Carbon (mg/L)	-0.08	0.17	-0.40*	0.38	-0.46*	0.19
Calcium (mg/L)	-0.36	-0.01	-0.30	0.57**	-0.54	0.34
Magnesium (mg/L)	-0.16	-0.02	-0.28	0.41*	-0.45*	0.31
Sodium (Na, mg/L)	-0.13	-0.03	-0.36	0.28	0.08	-0.01
Potassium (K, mg/L)	-0.36*	-0.37*	-0.094	0.53**	0.09	-0.21
Sulfate (SO_4, mg/L)	-0.01	0.20	-0.25	0.16	-0.01	0.27
Alkalinity (mg/L as $CaCO_3$)	-0.32*	-0.13	-0.19	0.55**	-0.48*	0.30
Bicarbonate (mg/L)	-0.32*	-0.13	-0.2	0.55**	-0.48*	0.30
Conductivity (μS/cm)	-0.33*	-0.10	-0.31	0.58**	-0.38	0.20
pH	-0.32*	-0.19	-0.08	0.47*	-0.29	0.20
Colour (mg/L Pt)	-0.04	0.35	-0.18	0.01	0.18	0.01
Chlorophyll-a (μg/L)	-0.19	-0.02	-0.32	-0.51**	0.47*	-0.33

**significant to 99th percentile, * significant to 95th percentile, + = transformed

At the lowland catchments, higher groundwater connection is occurring as a result of high peatland cover, which lends to high conductivity and dominant cation concentrations. Fens, more commonly found in these lowland systems, and are known to have stronger connections to local groundwater systems (Halsey *et al.* 1997). Allen *et al.* (2003) attributed this effect to altitude and similarly, in this study, elevation was negatively correlated with all major ions and conductivity (see Table 2.4). Regression analysis also indicated that elevation accounted for 73% (Fig. 2.5) of the variation observed in conductivity. However, elevation is spurious correlated and it is likely that elevation is a representative measure of the amount of groundwater input occurring within systems. The Birch Mountains also receive moderately high conductivity and more major ions, attributed by Halsey *et al.* (1997) to the influence of permafrost features, such as the collapse scars found in catchment BM4. However, this hypothesis is not considered to be the over-riding influence, rather at the Birch Mountain sites, deep lakes are likely connected to regional aquifers and thus receive groundwater input, and associated increased conductivity levels and concentrations of major ions.

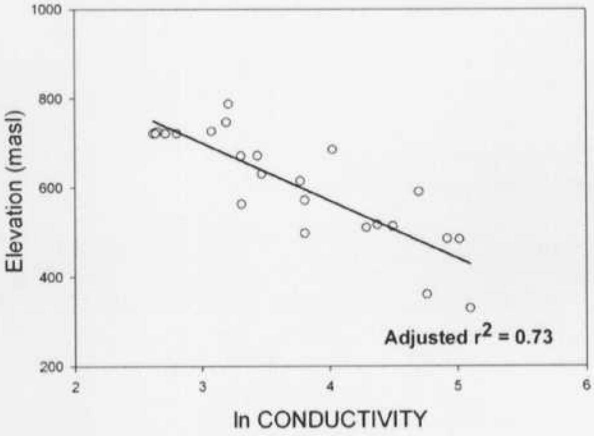

Figure 2.5 Spurious relationship between conductivity and elevation (r^2 = 73%). Open circles illustrate lake sites (n = 25).

pH was also significantly lower in the high water-yield lakes, and most notably so in the Stony Mountain systems. Regression analysis indicated that 36% (P = 0.01) of the variation observed in pH was due to deciduous forest cover and drainage basin area. Prepas *et al.* (2001) associated the occurrence of bog features in catchments with low pH, alkalinity and base cation concentrations. Bogs were negatively correlated in this study with Ca (r = -0.54, P < 0.01), Mg (r = -0.45, P = 0.04), alkalinity (r = -0.48, P = 0.02) and bicarbonate (–0.48, 0.02). High amounts of bogs in the Stony Mountains could be inputting acid humic waters, which could be increasing lake sensitivity.

Forest cover in this case may be spurious, because deciduous forest covers occurred primarily in the lowland catchments, which were shown to have groundwater inflows from peatlands. In the cases where drainage basin area increased, the peatland percentage of the watershed also likely increased, which also would favour higher inputs of groundwater and greater buffering capacity. pH buffering at the Birch Mountain sites (high water-yield), similarly, may have occurred due to moderate cation availability input groundwater inputs from connections to regional aquifer systems (Halsey *et al.* 1997). Also in these high water-yielding systems, large drainage basins and steeper slopes can provide a constant input source of acidic buffering materials (McEachern *et al.* 2000). pH buffering may also be occurring in Birch Mountain systems as a result of moderately high DOC and colour relationships (see discussion in the following section).

Overall, it appears conifer-dominated catchments of the uplands have lower DOC, and higher DOC occurs in the lowland sites (as observed in West Fort McMurray systems). Regression analysis revealed that DOC varied as a result of forest cover type and catchment to lake volume ratio (adj. $r^2 = 77\%$). DOC was also correlated with DR, as was the case for other lakes studied on the Boreal Plain (Prepas *et al.* 2001, McEachern *et al.* 2000). Both Prepas *et al.* (2001) and Pienitz *et al.* (1997a) observed a stronger connection between vegetation and DOC in watersheds where wetlands comprise a greater percentage of the catchment area. Regression analysis revealed DOC-vegetation relationships in this study were strongest in the low water-yield, wetland dominated catchments ($r^2 = 53\%$, $P = 0.01$). The poor fens adjacent to upland vegetated slopes occurring at lowland sites may translate DOC-laden water continually to the downstream end, affecting carbon levels in receiving lake waters (Halsey *et al.* 1997). Or, DOC processes could be affected by lake size, similar to results observed by Engstrom (1987).

On the other hand, DOC delivery in the uplands systems may be influenced by the hydrologic cycle. DOC is strongly associated with net catchment to volume ratios ($r = 0.83$, $P << 0.00$), water -yield and drainage ratios. In the Birch Mountains, the groundwater connections could also be lending to increased DOC in these systems. The Stony Mountain lakes and catchments, where lakes with higher water-yields, lower drainage ratios, and low net catchment/perimeter to volume ratios occur, have lower DOC contributions from catchments and possible reduction of DOC in the water column owing to moderately long water retention times.

Mean average colour in study lakes was 147 (mg/L Pt), with minimum and maximum values of 11 and 485 mg/L Pt, respectively. Colour in our study lakes is greatest in the Birch Mountains and in NE Fort McMurray. Lake colour in other studies on the Boreal Plain was higher on average in wetland-dominated catchments, but lower on average as a whole than our study lakes (Prepas *et al.* 2001). Studies of lakes in the Caribou Mountains indicated these sites had very high colour (236 mg/L Pt; McEachern *et al.* 2000), while colour for lakes in southern Alberta (Swan Hills) was low in comparison (46 mg/L Pt, Allen *et al.* 2003).

In our study lakes, colour had a strong, negative relationship to residence time (Table 2.4); this is consistent with findings that suggest that colour degrades with greater residence time owing to its origin in humic matter (Rasmussen *et al.* 1989). Regression analysis indicated that wetlands and slope were responsible for an additional 35% of the variation found in colour in these watersheds (over the 20% caused by residence time alone). Colour was also correlated positively to DR, indicating that colour may be affected by the size of the drainage basin contributing area, concurrent with findings that colour is associated with humic matter and that larger catchments tend to export more humic matter, especially if they are wetland-dominated (Prepas *et al.* 2001).

Colour was lowest in the Stony and West Fort McMurray systems, where water residence times were of moderate length and DR was lower (compared to the Birch Mountains or NE Fort McMurray systems), it seems that these factors combined to lower colour in these systems despite high wetland coverage in these areas. It should be noted that systems like WF3 and SM4 are exceptions to the regional averages. These systems are over 90% bog and have extremely high colour, indicating the peatlands in this region contribute colour to lakes when represented by high percentages of the overall cover type in watersheds (Prepas *et al.* 2001).

In the high water-yield systems, it appears that increased proportion of wetlands was the main driver in colour relationships, accounting for 59% (adj. r^2) of variation. In low water-yield systems, where wetlands were already a major component of the landscape, colour export increased with increased drainage ratio, perhaps owing to a greater amount of water influx, and a higher contribution from wetlands systems found within the drainage basin.

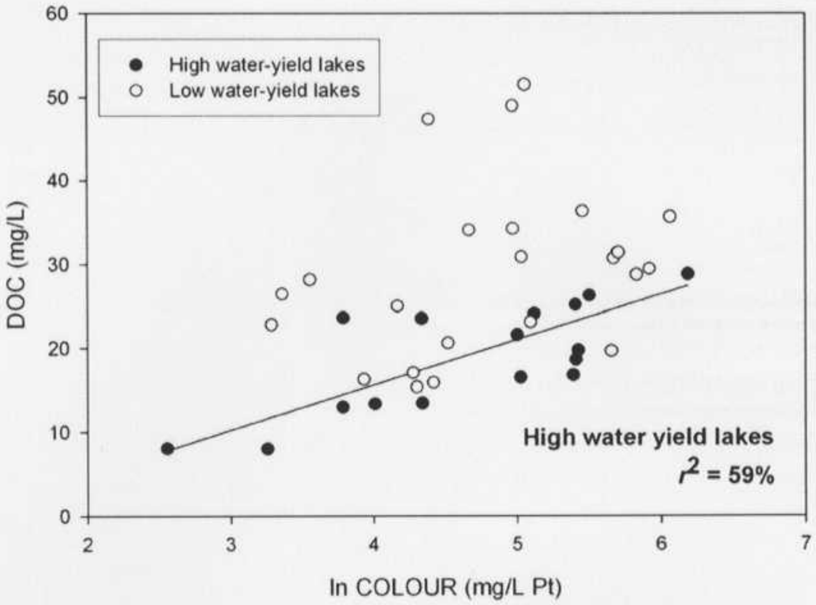

Figure 2.6 Relationship between DOC and colour in high and low water-yield systems (r^2 = 59%).

Colour and DOC were weakly related in the data set as a whole (*r* = 0.53, P<<0.00), but a linear regression revealed that a strong relationship existed between these factors (r^2 = 59%) when only high water-yield systems data were considered. In contrast, the relationship was not significant in low water-yielding systems (Fig. 2.6). In high-water-yield lakes, colour and DOC are associated with the delivery of water to lake systems, possibly allowing humic matter to be transported through the catchment (Rasmussen *et al.* 1989). This could be attributable in the high water-yielding systems to slope factors (Engstrom 1987); colour in this study is not correlated to slope in the data set as a whole, however slope does affect colour export (r^2 adj. = 55%) in high water-yield lakes (Fig. 2.7). This indicates that slope and colour form a detectable relationship only in steeply sloped, upland-dominated catchments, where high water-yields are delivering coloured water to lake systems (Rasmussen *et al.* 1989).

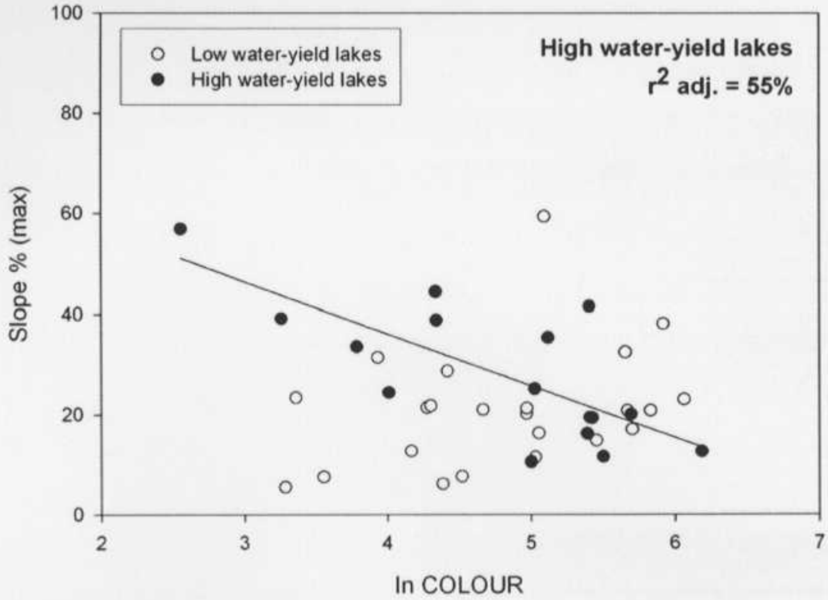

Figure 2.7 Relationship of slope to colour in high and low water-yield lake systems. The black circles are the high water-yield lakes and the low water-yield lakes are shown with open circles. The regression line illustrates the relationship between slope and colour at the high water –yield lakes only ($r^2 = 55\%$).

TN and TP relationships suggest that nutrients in these systems are driven by a combination of water-yield, catchment morphology and vegetation coverage, including the percentage of peatland in catchments. The highest average value for TN was recorded in West Fort McMurray systems (2051), almost twofold average TN values for systems in the Birch Mountains (1250); average TN for all study catchments was 1325. TN values in our watersheds were higher than have been found in other areas, including in the boreal systems located in the Yukon (Pienitz *et al.* 1997), in lakes in the Caribou Mountains (McEachern *et al.* 2001) and in those on the Boreal Plain (Prepas *et al.* 2001). TN relationships in study catchments are inversely correlated to water-yield ($r = -0.62$, $P<<0.01$), R/P ($r = -0.56$, $P<<0.01$); this is similar to results found by Prepas *et al.* (2001).

TN declines with increased water-yield (strongest in the high water-yield lake set r^2 adj. = 62%) and lake depth, either through the flushing of nutrients in runoff moving over the landscape (compared to input P) or through in-situ lake dentrification (Kalff 2002b). Negative correlations found between TN and maximum depths for Boreal Plains lakes and in other regions (Prepas *et al.* 2001, D'Arcy and Carignan, 1996) suggest that TN may be degraded in deeper systems. TN export in lowland systems was more pronounced in the small, shallow lake systems with deciduous headwater catchments, such as those located in West Fort McMurray. Here the wetlands and associated water-logged soils are effective translators of nitrogen to shallow lake systems in this region (Prepas *et al.* 2001).

TP relationships in catchments are highest in the Birch Mountains (mean 105) and lowest in NE Fort McMurray, with an average value of 64 for all systems. The Stony Mountains and West Fort McMurray have average values of TP close to the data set average, while NE Fort McMurray has concentrations that are twofold lower. Values are higher than those in more northerly Boreal Forest studies (Moser *et al.* 1998), as well as in southern Boreal Plain lakes situated in agricultural zones (Mitchell and Prepas 1990); and they are slightly higher than those found in the Caribou Mountains and in other Boreal Plain lakes (Prepas *et al.* 2001).

Positive relationships based on Pearson's correlations were detected between bog systems ($r = 0.50$, $P<0.01$) and TP, while negative relationships were observed between lake depth ($r = -0.42$, $P<0.01$) and conifers ($r = -0.42$, $P<0.05$). These relationships were also reflected in regression analysis. It appears that TP is being exported by bogs and concentrated in upland catchments of the Birch Mountains ($r^2 = 44\%$). Very deep systems, on the other hand, may experience degradation of TP in the water column. Wetland systems, especially fens, may be sequestering TP (Prepas *et al.* 2001); this is indicated by the more moderate TP averages of West Fort McMurray, the low values in NE Fort McMurray systems and the negative correlations between TP and fens in low water-yield systems ($r = -0.55$, $P = 0.05$). TP concentrations have also been linked to geologic variations that aid in soil development (shales; Pienitz *et al.* 1997a), although a relationship between TP and catchment geology or vegetation was not considered to be a factor in TP production in lake systems by Moser *et al.* (1998). Chlf-*a* is closely linked with both TP ($r = 0.73$, $P<<0.01$) and TN ($r = 0.65$, $P<<0.01$) in these systems, likely a result of available nutrients. Chlf-*a* was most strongly linked to the presence of wetlands in both high and low water-yield systems ($r = 0.66$, $P<0.05$).

VI. Conclusions

Regional interactions between hydrology, land cover and lake water chemistry revealed complex interactions occurring within Boreal Plains catchments. Upland and lowland sites were compared; lowland sites tended to have lower water-yields, and were dominated by headwater deciduous forests adjacent to fen systems. Upland sites tended to have coniferous forests, greater lake volumes surface and drainage basin areas and bog-dominated covers. Low water-yields found at the lowland sites may occur due to low transmission occurring across shallow slopes, and impedance from features such as beaver dams (McEachern *et al.* 2005). In general, the lowland sites contained stronger connection to groundwater as a result of increased inputs from the prevalence of wetland features such as fens. Groundwater connection was also occurring at the upland locations where deep lakes may come into contact with regional aquifers, especially in the Birch Mountains. Permafrost or soil freezing could also be creating higher runoff in these bog-dominated catchments via overland runoff processes that occur during spring freshet when soils are still frozen. Further analysis and more in-depth study of these catchments is required to fully understand the hydrologic patterns observed within these lake systems.

Regional lake water chemistry was variable, and supported the hypothesis that groundwater contributions were more prevalent at the lowland sites and allowed for higher levels of conductivity and a greater concentration of major ions at these lakes. Upland lake sites had lower conductivity and a lower concentration of major ions, but at the Birch Mountain sites, deep lake systems may be receiving inputs of groundwater that could be contributing to input of these constituents. Higher DOC in the sites in West Fort McMurray may also be owing to smaller, shallower lakes systems with moderately long water residence times (WRS 2004). DOC and colour were high in the upland sites, and regression analysis showed that the presence of bogs was influencing DOC within these catchments. Despite high bog coverage at the Stony Mountain sites, DOC is lower at these sites possibly owing to longer water residence time and higher water storage in the eolian sandy/silt matrices common to the region.

Nutrients and biotic variables appeared to be most closely related with upland sites where groundwater inputs and permafrost coverage was a possibility (Birch Mountains);

however. In this study, water-yields and lake depths play a key role in flushing and degrading nitrogen in the lakes, which is why lakes in NE Fort McMurray have low nutrient levels. Phosphorus was exported by bog systems and sequestered by fens, as found by other workers. Lake depth may also play a role in decreased phosphorus availability at lake sites.

Assessment of acid-sensitive systems is difficult because of the complex and varying interactions present within landscape, lake hydrology and water chemistry. Suggestions that small ponds and sites may be sensitive to acidic inputs may not apply because these types of lakes are also located in lowland zones and have connections to groundwater that allows for inputs of buffering cations and calcium, which should offset acidic inputs and/or concentration of strong acid anions (Kalff 2002a). Additionally, high groundwater inputs, which refresh lake water in these systems, may offset strong acids generated by bog coverage in catchments located in the upland regions. Bogs can also act to lower acid-sensitivity via the input of weak acids, which form protective barriers from UV penetration and acid transformation in lakes. Thus, lowered acidity in the bog systems of the Birch Mountains is not occurring, whether it is due to the association of buffered input water from groundwater inputs, or protection by DOC and colour inputs in these systems; pH values are similar to precipitation in this region. Halsey *et al.* (1997) hypothesized that these systems had not been affected by input of sulphur and nitrogen from associated oil sand operations, and also projected that due to the location and to overriding wind patterns, acid-sensitivity in the Birch Mountains may not be an issue with increased development.

Low values of pH in systems of the Stony Mountains, however, may be indicative of acid-sensitivity, which could be influenced by increased acid inputs from oil sands developments. The Stony Mountains are more evaporative, have lower drainage ratios, and longer water residence times than systems located in the Birch Mountain uplands. Major ions such as calcium, alkalinity and bicarbonate are low, providing no buffer to acidic inputs. Additionally, although dominated by bog systems, these systems have low DOC contributions, owing perhaps to in-situ degradation of DOC within the lake based on water residence times or to a low net catchment to volume ratio. Therefore, buffering by weak acids associated with DOC is also not occurring. This lack of buffering capacity may result in higher lake sensitivity to increased acidic contributions from oil sands operations.

VII. Recommendations

This study reviewed lake water chemistry and its relationship to both hydrology and physical features at lake sites. These factors combine in some instances to increase the probability that atmospheric inputs of sulphur and nitrogen generated via oil sands operations and processing will impact the lake systems of the Stony Mountains to such a degree that lake water quality could degrade. The 0.17 keq H^+/ha/yr acidifying input isopleths (Fig. 2.1, Shell 2005) that bisect the Stony Mountains indicate the proximity of acid-generating operations to these upland lake sites. Therefore, systems within the Stony Mountains have been targeted as acid-sensitive based on critical acid loadings and an exceedance assessment (Chapter 3). Even though this is the case, the AOSERP data set (Abboud *et al.* 2002) does not include complete coverage of any of the Stony Mountain catchments examined in this study. Recommendations include that soils mapping be extended to this region, and that detailed study of wetlands be undertaken for this region to fully document and model acid-sensitivity at these sites.

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Chapter 3 : Refining estimates of water-yield for critical loadings assessment: an isotopic approach

Abstract

A stable isotope technique for estimating water-yield is developed and applied to assess critical acid loadings to 49 lakes and ponds in hydrologically-complex, wetland-rich terrain of northeastern Alberta. The results from this case study, which include detailed comparisons with an earlier assessment using conventional hydrometric station data, indicate that the technique has broad applicability to estimations of water-yield and loadings potential within ungauged lake basins. Comparison of the method with regional hydrometric data suggests very similar results in moderately-sized watersheds, although isotope-based estimates appear to capture an improved view of water balance variability within small-scale systems. The isotope mass balance method is notable for its ability to predict the water-yield and critical loads despite only three years of water sampling, as well as for its ability to characterize hydrologic variability across regions and among specifically targeted study basins. For aquatic ecosystems of northeastern Alberta, an area expected to be affected by acid deposition from regional oil sands development, the results show clearly that nearby lakes often have dissimilar water residence times, throughflow rates, and catchment water-yields: factors that significantly affect the acid-sensitivity of individual lakes.

I. Introduction

Previous studies (e.g., Erickson 1987) have indicated that lakes and ponds in northeastern Alberta may be sensitive to acidification, due to the prevalence of acid-sensitive soils and aquatic features common to the region (see also Schindler 1996). Increasing development in the oil sands area and commensurate increases in NO_x and SO_x emissions are now raising additional concerns regarding acidification of sensitive soils and aquatic ecosystems. Reduction in emissions carries potentially costly implications for existing operations and for new development projects if critical loads are exceeded. Much of what is known about critical acid loads (CL_A) in the area is based on calculations by WRS (2004) for 449 lakes and ponds in the region using the Steady-State

Water Chemistry model (SSWC) of Henriksen *et al.* (1992). The SSWC model application showed that 10 lakes exceed critical loads, but with considerable uncertainty due to a number of poorly known factors, including base cations estimates, acid-neutralizing capacity and water-yield. Water-yield is a more significant unknown in northern Alberta due to the sparsity of the hydrometric network and, shown, the high lake-to-lake variability in runoff, which reduces the accuracy of interpolating between gauging stations.

Accuracy of the critical acid load estimate relies to a large extent on accurate estimates of water-yield (W_Y). As demonstrated, use of in situ isotope measurements provides a sharper focus on water-yield than conventional hydrometric monitoring in the area and is useful for assessing sensitivity of individual lakes to acid deposition. For a regional subset of the 449 previously studied systems, an isotope mass balance technique was applied using ^{18}O and ^{2}H similar to that of Gibson *et al.* (2002), which utilizes the systematic isotopic fractionation that occurs during evaporation to estimate the rate of throughflow to the lake, the lake residence time, and the required water-yield from the catchment to sustain the observed isotopic balance. Results of the isotopic approach are compared to those from conventional hydrometric techniques in order to demonstrate the implications for critical acid loading models to illustrate potential errors and limitations in the approaches, and to offer insight into scale-dependent landscape features that affect the way in which water is processed and removed from the landscape in Boreal Forest terrain.

The objectives of this paper are to present the water-yield and the CL_A results from the two methods and to discuss why the results are similar at some sites and different at others. The results from this analysis are anticipated to be useful for: (a) identifying potential errors and limitations in lake-specific CL_A calculations from available, regionally-representative, hydrometric station data; (b) determining landscape characteristics that may support a broad approach versus a detailed approach (c) developing insight about relationships between broad-scale and small-scale catchment parameters that may affect hydrologic regimes in boreal watersheds; and (d) improving understanding of the impact of scaling down hydrologic estimates to the headwater basin level within these landscapes.

II. Site Description

The lakes under study are located in northeastern Alberta, Canada (55° 30' N to 60°N 30'W, Fig. 3.1). Thirty lakes are situated within 200km, indicated in Fig. 3.1 as the grey zone around the town of Fort McMurray and its nearby oil sand developments. Five lakes are found in the Caribou Mountains and four lakes are situated above Lake Athabasca. All are primarily located in headwater catchments and range in size from shallow, small ponds (1m deep, < 0.5 km^2) to large lakes (30m deep, 43km^2), with average lake depth and size equal to 4.3m and 3km^2, respectively. The lakes were initially a component of exploratory work on acid-sensitive lakes in Alberta, and were selected for further study based on their water chemistry (RAMP 2004).

Annual thirty-year air temperature normals (1971–2000) at Fort McMurray are 0.7° C, while the average open-water season (May to October) temperature is 11.6° C. Mean annual precipitation is 456 mm, 69% of which falls as rain during the May to October period (MSC 2004). Average annual evaporation is 480 mm (Hamon 1961, New *et al.* 1999), while evaporation from lakes is estimated at 578 mm (Bothe and Abraham 1987, 1993). January relative humidity is 75%, while in July it is 70% (New *et al.* 1999). A detailed discussion of the issues related to the use and applicability of this climate data and its use in the model is provided in Chapter 1. Additionally, both Chapter 1 and 2 include discussions on the validity of long-term averages and the relationship between the long-term averages and the three years of study.

The lakes are grouped within six regional study areas, namely, (1) Northeast (NE) Fort McMurray, (2) Stony Mountains, (3) West Fort McMurray, (4) Birch Mountains, (5) Caribou Mountains and (6) Shield Lakes. Study areas range in elevations from 200m (Region 6) to 1000m (Region 5), with similar average elevations occurring within Regions 1 and 3, and within Regions 2 and 4. Average slopes (based on DEM analysis in a Geographic Information System) within study catchments are low, ranging from 0.5% in Region 3 to 5.4% in Region 5, with higher average slopes occurring in the watersheds of Regions 5 and 6 versus 1 and 2. There is a wide range of variation present within the lake sites, including their latitudinal position, morphometry, and the landscapes within which they are situated (Table 1).

Regional surficial materials consist primarily of thick tills (65%), till veneers (21%), with some coarse sands and silts (3%) and minor amounts of sands and gravel, as well as fine silts and clay (Geological Survey of Canada 1995). Soils in Regions 1, 2, 3 and 4 are comprised of Organics, Luvisols, Brunisols and Cryosols (Region 4), while Cryosols and Regosols are dominant soil types in Regions 5 and 6, respectively (Agriculture Canada 2004). Permafrost is sporadic discontinuous (10–50%) with low ground-ice content (<10%) in Region 5 and 6 (Taiga and Shield) and in the remainder of the sites, permafrost is either absent or only in isolated patches (0–10%), with low or low-to-nil ground ice (Brown *et al.* 1998). The overall study area comprises 13% bogs, 22% fens and 65% mineral upland. Peatland coverage in specific watersheds varies but the average amounts are very similar to average values for the region at large (Vitt *et al.* 1996).

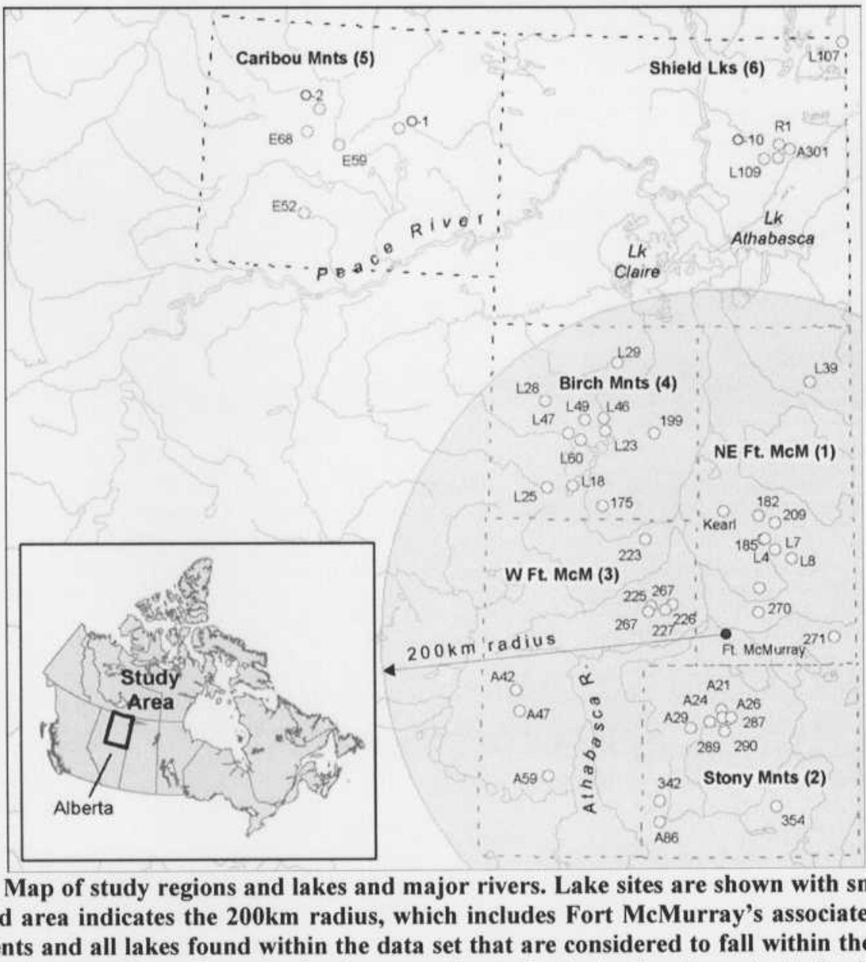

Figure 3.1 Map of study regions and lakes and major rivers. Lake sites are shown with small circles. The shaded area indicates the 200km radius, which includes Fort McMurray's associated oil sands developments and all lakes found within the data set that are considered to fall within the area most likely to be impacted by oil sands development. Inset illustrates location of site in Alberta and Canada.

Table 3.1 Lake number, region, coordinate, lake area (km^2), and drainage basin area (DBA, km^2) for study sites. Latitude and longitude are given in decimal degrees (dd).

Lake Number	*Region*	*Latitude (dd)*	*Longitude (dd)*	*Lake Area (km^2)*	*DBA (km^2)*
NE1	REGION 1	57.15	-110.85	0.7	13.8
NE2	NE Ft. McMurray	56.64	-110.20	4.2	31.9
NE3		57.29	-111.24	5.8	74.7
NE4		57.09	-110.75	0.3	17.3
NE5		57.05	-110.59	0.6	7.2
NE6		57.69	-110.40	1.2	17.1
NE7		56.89	-110.90	1.9	21.5
NE8		57.27	-110.90	0.4	11.1
NE9		57.15	-110.86	0.1	4.2
NE10		57.23	-110.75	0.1	6.6
NE11		56.77	-100.91	3.2	23.2
SM1	REGION 2	55.76	-110.76	2.4	9.5
SM2	Stony Mountains	56.26	-111.26	1.4	18.7
SM3		55.79	-111.83	2.0	26.3
SM4		56.20	-111.37	1.9	6.4
SM5		56.15	-111.23	0.5	12.5
SM6		56.17	-111.55	1.1	7.4
SM7		56.22	-111.17	0.7	4.1
SM8		55.68	-111.83	1.5	7.3
SM9		56.21	-111.20	1.9	11.6
SM10		56.22	-111.25	1.1	10.5
WF1	REGION 3	56.35	-113.18	3.2	27.4
WF2	West Ft. McMurray	56.24	-113.14	0.8	24.1
WF3		55.91	-112.86	2.2	40.3
WF4		57.15	-111.98	0.0	1.8
WF5		56.80	-111.92	0.2	7.1
WF6		56.81	-111.72	0.2	5.3
WF7		56.78	-111.79	0.1	1.8
WF8		56.77	-111.95	2.0	29.1
BM1	REGION 4	57.41	-112.93	17.0	68.3
BM2	Birch Mountains	57.31	-112.40	0.4	5.5
BM3		57.69	-111.91	0.1	1.5
BM4		57.42	-112.69	44.0	163.6
BM5		57.65	-112.62	1.0	29.6
BM6		57.69	-112.74	4.3	38.4
BM7		57.76	-112.58	2.6	30.5
BM8		57.85	-112.97	1.3	19.7
BM9		58.06	-112.27	0.7	8.5
BM10		57.77	-112.40	1.2	33.9
BM11		57.70	-112.38	3.5	33.7
CM1	REGION 5	58.77	-115.44	1.6	25.5
CM2	Caribou Mountains	59.13	-115.13	9.6	47.5
CM3		59.19	-115.46	2.3	27.6
CM4		59.31	-115.35	2.6	38.4
CM5		59.24	-114.53	0.6	3.1
S1	REGION 6	59.72	-110.02	3.4	16.8
S2	Shield Lakes	59.12	-110.83	1.0	111.3
S3		59.19	-110.68	1.4	31.1
S4		59.17	-110.57	1.4	124.5
S5		59.13	-110.69	0.3	4.8

III. Methods

Water samples were collected from 2002 to 2004 in the late summer/early fall. Lake samples were collected from the pontoon of a fixed-wing aircraft and helicopters were used to access ponds and terrestrial monitoring sites. For lakes greater than 2m in depth, a composite water sample was collected at the deepest part of the lake by multiple hauls of a polyvinyl chloride tube to the euphotic depth (2 times the secchi disk depth) or 1m above the lake bottom. For lakes less than 2m deep, a composite sample was created from five one-litre collections at 0.5m depths from different locations around the lake. Water was transferred from the composite sample to a 30mL airtight high-density polyethylene container and sent to the University of Waterloo for standard analysis of stable isotopes $\delta^{18}O$ and $\delta^{2}H$ by mass spectrometry within two weeks of field data collection. All δ isotope results are given in permil (‰) vs. V-SMOW (see Coplen 1995).

Watershed and lake physical parameters were estimated in a Geographic Information System (GIS) using 1:10,000 orthophotography and digital elevation models (DEMs) (1:20,000) to digitize lake surface area, drainage basin morphometry, and lake surface elevation. Lake bathymetry was measured at three to five multiple transects across lake sites, using a sounder to record depth at equal time intervals while traveling at a constant speed and bearing between initial and terminal positions, which were recorded using a Garmin hand-held global positioning system (GPS). This information was transferred into the GIS and interpolated to create depth polygons of varying intervals. Lake volume was calculated based on the surface area of slices at discrete depth intervals using a limnological frustral equation (P. McEachern, pc). Lake centroids based on surface areas were used to generate specific latitude and longitude positions for interpolation of variables such as temperature from gridded climate data sets. Drainage ratio (DR) as referred to here is calculated using the results from the small-scale watersheds GIS analysis (lake area/drainage basin area), and for large-scale watersheds the CEMA stream network linework (CEMA, 2003) data (stream length/drainage basin area) was used. Slope was derived using 1:20,000 DEM tiles, mosaiced and analysed using Spatial Analyst functions. For the drainage ratio analysis, stations were removed when the broad scale data was not available or incomplete (L39/07DD002; L8, 185, L4/07DC001).

Water-yield ($\mathrm{mm{\cdot}yr^{-1}}$) was generated using an isotopic water-mass balance model (IMB), developed under the assumptions of (1) complete vertical mixing, (2) constant density of water and (3) steady state conditions ($\Delta V/\Delta t = 0$, $\Delta\delta/\Delta t = 0$, where V = volume and t = time), expressed as:

$$(1)\quad P\delta_P + W_Y\delta_{WY} = Q\delta_Q - E\delta_E\,,$$

where P is total precipitation ($\mathrm{mm{\cdot}yr^{-1}}$), δ_P is the isotopic composition of precipitation, W_Y represents lake inflow and its isotopic signature ($\delta_{WY} \approx \delta_P$ for local conditions and time-scales appropriate to the annual water balance), Q equals the lake outflow (surface water and groundwater) represented by the mean (n = 3 yrs) lake water isotopic composition (δ_L, where $\delta_Q \approx \delta_L$), and E equals the total lake evaporation in $\mathrm{mm{\cdot}yr\text{-}1^{-1}}$ (the isotopic composition of evaporated moisture). δ_E was estimated using a 1-D diffusion model (Craig and Gordon 1965) and the relationships between temperature, humidity, the isotopic composition of atmospheric moisture, δ_A, and isotopic fractionation effects (as illustrated in Gibson 1993 and Gibson *et al.* 2002). Fractionation effects (ϵ, ϵ^* and ϵ_K, total isotopic separation, equilibrium and kinetic fractionation) are constrained based on laboratory experiments that related fractionation to humidity, temperature, boundary-layer transfer processes (turbulence) and molecular-diffusion coefficients (Horita and Weslowski 1994, Gonfantini 1986). δ_A was calculated by coupled scaling of the equilibrium isotopic separation values for oxygen and hydrogen (ϵ^*) to achieve a best-fit to the slope of the regional δ^{18}O-δ^{2}H evaporative enrichment trend, thereby accounting for seasonality effects (see Gibson 2002).

The evaporation-inflow ratio (x) can be substituted into Eq. [1] and rewritten for steady-state systems as illustrated in Eq. [2]. Within the context of the isotopic water balance, x can be computed as an expression of the limiting isotopic enrichment (δ^*) of a lake, and the gradient of that enrichment, m, as shown in Eq. [3].

$$(2)\quad \mathrm{x} = \frac{\mathrm{E}}{\mathrm{P + W_Y}},$$

$$(3)\quad \mathrm{x} = \frac{(\delta_L - \delta_P)}{\mathrm{m}(\delta^* - \delta_L)},$$

The computations for isotopic atmospheric effects (δ_A, δ^*, h and m, where h is relative humidity in percent) must be weighted by the monthly evaporative flux to emphasize variability in E (see Gibson 2002).

Climate variables can be estimated using station data from an established network although this is only possible when long-term records are available at appropriate resolutions across the regional study area. Therefore, climate variables were estimated for each site from gridded climatological data sets (30 years, 1961–1990). The limitations on the use of these data and drawbacks of applying downscaled gridded station data at this level are discussed in Chapter 1. Precipitation was estimated from the CRU half-degree data set (New *et al.* 1999). E was calculated using a Hamon approach (Hamon 1961, New *et al.* 1999). Temperature and relative humidity were approximated based on the CRU 10-minute climatology (New *et al.* 2002).

Water-yield ($\mathrm{mm \cdot yr^{-1}}$) was calculated for the net catchment area at 50 lakes using the output results from Eq. [3], and precipitation and evaporation over the lake interpolated at each lake site.

$$(4) \quad W_Y = \frac{E}{x} - P ,$$

The comparative approach to estimating water-yields utilizes the average, long-term W_Y data ($\mathrm{mm \cdot yr^{-1}}$) from 21 WSC hydrometric gauging stations, grouped by representative watershed region. The stations used in this analysis included both active and discontinued stations (62% and 38%, respectively). Most of the gauges (82%) are seasonally operated (March to October), while all of the continuous stations used for this analysis have been deactivated. Where gauges occur within WSC watersheds, they are referred to in this paper as being gauged downstream, as opposed to the instances where gauges from nearby or adjacent watersheds were used to estimate water-yield. None of the headwater study lakes were gauged directly from outlets located within catchment bounds. As well, in cases where the gauges were operated for short periods of time (e.g., less than 10 years) the data were not used even when the station was closest to the lake site. The WSC hydrometric stations used in this study had an average collection record of 27 years.

Critical loadings (keq H^+/m/yr) were calculated using the W_Y ($mm \cdot yr^{-1}$) to express the value as a flux (mass/time) of the annual average net catchment runoff (WRS 2004):

$$(5) \quad CL_A = ([BC]_0 - [ANC\,lim]) * W_Y / 10^5 ,$$

where BC_0 is the non-marine flux of base cations concentrations assumed to be equivalent to the sum of base cations in current lake water samples, W_Y equals runoff or water-yield ($mm \cdot yr^{-1}$), and ANC_{lim} is the critical acid-neutralizing capacity limit, in this case corresponding to a pH of 6.0 where biotic effects from acidification have been shown to occur (75 μeq/L for all lakes, WRS 2004). The isotope mass-balance model assumes the lakes are operating at steady state and applies the use of water quality data from the late fall season, which is considered representative of annual average lake water chemistry (Henriksen and Posch 2002). Bicarbonate is considered the primary buffering source for lakes, and surface runoff from the catchment is the only source of alkalinity (WRS 2004).

Exceedance occurs when the acid-generating processes are greater than the acid buffering processes in lake systems. Exceedance is based on a potential acidifying input (PAI) scenario (as described in WRS 2004) and quantifies the number of affected aquatic features occurring within a region. The PAI scenario used in this analysis is based on the basic, baseline assessment undertaken by Alberta Environment (Cheng *et al.* 1997). When CL_A is smaller than the PAI value, the lake is considered exceeded and therefore at risk of acidifying to a degree harmful to a biological indicator species. It is recognized that PAI values are controversial in their assumptions and calculation, and some workers have opted to use alternate method to measure exceedance (Shell 2005). However, PAI-based acid-sensitivity estimates are included in this chapter to illustrate the importance of accurate calculation of water-yields for input into critical loadings estimates, on which exceedance scenarios are built. The RAMP committee currently applies this method to assess acid-sensitive lake systems in the region. The last section of this paper discusses the potential for uncertainty in W_Y and CL_A calculations that may influence political and social decision-making processes.

Depending on the availability of hydrometric and lake chemistry data, subsets of the 49 lakes were created for hypothesis testing. When comparing the two approaches for water-yield calculation, lakes in Regions 5 and 6 were not used for comparative analysis, as broad-scale data were sparse within these regions. In most instances the closest hydrometric station gauge was used to estimate the depth of runoff in the watershed, but for some cases examination of landscape and morphometry at IMB and WSC catchments led to the selection of two nearby gauges and use of the average depth of runoff to represent the estimate of W_Y. The watersheds where WSC water-yields were input as an average of flow from two hydrometric stations were excluded because it required averaging of watershed features which may have skewed results at sites where the two watersheds had vastly different characteristics (such as at CM3 and in all of Region 4 and 5 stations). The exception to this was BM10, where WSC-water-yield was calculated as an average of two hydrometric stations found in comparable basins. In this case, the results of feature analysis from both basins were averaged. S4, originally part of the regional subset ($n = 50$) was not included in the critical acid loading analysis ($n = 49$) because data for BC_0 does not yet exist. Some WSC watersheds, including 07JB002, 07KE001, 07DC001, and 07DD002, did not have complete coverage for data sets, and were therefore excluded from comparative analysis.

Water-yields estimates were high for the four largest and deepest lakes systems in the data set (CM2, S1, BM1, and BM2 average aerial extent equals 18.5 km^2 compared to data set average of 3 km^2, average maximum depth 17.5 m vs. 4.3 m for the data set average maximum depth). These lakes that may come into contact with groundwater flow via interception with regional aquifer systems. The isotope mass-balance model incorporates both groundwater and precipitation input sources as a combined term as groundwater often reflects long-term isotopic composition of precipitation within hydrologic systems (see Fritz *et al.* 1987). This finding revealed that the isotope mass-balance method could be used to identify such connections occurring within lake systems. However, for some analysis, these four lakes appear to be outliers, and therefore were removed for analysis to determine the nature of relationships without the influence of these very large, deep, groundwater-driven lake systems.

Due to the lack of detailed soils information for much of this study area, the soils data were not used in the comparative analysis. The Alberta Peatland Inventory information was applied in this study to estimate wetland and upland coverage, although given its coarse scale, it is not entirely appropriate for this type of analysis and results should therefore be treated as rough approximations. This data set should be improved in future studies at these sites.

IV. Results

Lake water balance data used in the IMB are consistent with regional averages and previous studies conducted in the area. The results from gridded climate data analysis indicate that lake surface evaporation (Hamon 1961, Kalnay *et al.* 1996) ranges from 391 to 462 mm·yr^{-1}, and precipitation from 345 mm·yr^{-1} to 478 mm·yr^{-1} at study sites across the region. These numbers correspond well with other data sources for the region that report evaporation and precipitation numbers between 400 and 500 mm·yr^{-1} (Environment Canada 1978), as previously outlined in this chapter. Latitude is also correlated with these evaporation estimates: at lower latitudes evaporation is higher and at higher latitudes evaporation is lower; this is evident in differences between the southern sites in the Stony Mountains (average 449 mm·yr^{-1}) and sites in Region 5 and 6 (Caribou Mountains and Shield Lakes, average 438 and 401 mm·yr^{-1}, respectively). Evaporation also exceeds precipitation (New *et al.* 1999) in this region by 7% on average, while catchment areas for runoff production exceed lake areas by 89% on average. Transpiration is estimated to be 36 – 50% of evaporation in this region (Abraham 1999). Evapotranspiration is therefore estimated at approximately 300 – 400 mm·yr^{-1} (Environment Canada 1978). Not accounting for groundwater inflows or recharge, average depth of runoff is expected to range from 25 to 200 mm·yr^{-1} per year (Environment Canada 1978) across sites in the region. Applying this information to the calculation of estimates for runoff ratios results in a range of 0.03 to 0.53. The runoff ratio derived using the IMB model falls between 0.01 and 0.55 (with outliers removed, see discussion in Chapter 1) and the WSC runoff ratio falls between 0.12 and 0.47. Water-yields range from 5–200 mm·yr^{-1} (with outliers removed) and 45 – 179 mm·yr^{-1} for the WSC method.

Water-yields derived using the IMB method are also validated by the range in lake area size, drainage basin area, and catchment characteristics that indicate variable hydrologic settings are present across the region's study basins (Prepas *et al.* 2001). The IMB and the WSC methods provide average estimates of water-yield within a reasonable range from the Hydrological Atlas of Canada approximation. However, generalized runoff ratios based on the Hydrologic Atlas are more closely reflected by the IMB model water-yields at lower ranges. Additionally, IMB results use field-based water sampling and a model to characterize the hydrologic water balance of ungauged systems that has been successfully applied in other regional studies (Prepas *et al.* 2001, Gibson *et al.* 2002). The WSC estimate, on the other hand, is not model–based, using information from stations at nearby stream nodes and generalizing water-yield across large basins, which is then scaled down to the sub-catchment level. For these reasons the IMB model is considered to be more accurate than the WSC method, and it is therefore used as the basis for accessing the accuracy of the WSC results in this paper.

Regional average evaporation over inflow (E/I%) rates and water-yield results are given in Table 3.2. E/I (%) is a throughflow index that can be used as a proxy for evaporation flux within lake systems; higher values indicate more evaporation occurring within those study regions. E/I ratios are highest for Region 3, which also has low water-yield. The WSC method generates higher water-yield for Regions 1, 2 and 3, while Regions 4, 5 and 6 have lower water-yields compared to the IMB results. Additionally, Table 3.2 shows the results of an examination of WSC station locations relative to study basins for the regional areas; Region 1 and 2 have higher percentages of their lake population gauged (82% and 40%), and have the closest approximations for water-yield, based on the average regional value derived for the WSC method versus the IMB model.

Table 3.2 Summary by regional area for E/I ratios, water-yields, critical loadings assessments (keq H+/ha/yr) and percent of watersheds in regional areas that contain a WSC gauge and were used for this analysis.

Regional Areas	E/I $\delta^{18}O$ (%)	WSC W_Y ($mm \cdot yr^{-1}$)	IMB W_Y ($mm \cdot yr^{-1}$)	WSC CL_A	IMB CL_A	WSC Gauged Sites
1	25	124	96	0.8	0.7	82%
2	48	137	82	0.2	0.2	40%
3	55	90	23	0.5	0.2	25%
4	28	97	168	0.3	0.5	27%
5	25	106	186	0.3	0.5	20%
6	24	45	80	0.2	0.5	0%

Lake catchments have specific regional characteristics (Table 2.1 in Chapter 2). Average lake areas for regions span from 1km^2 to 7km^2. Lakes on average are smallest in Region 3, followed by 2 and 1, respectively, and are increasingly larger in Regions 6, 5, and 4. Drainage basins are also smaller in Regions 1–3 versus Region 4, 5, and 6. Volumes follow a similar pattern: Region 3 lakes are lowest in volume, followed by Regions 2 and 1, while Regions 4, 6, and 5 lakes (in that order) are highest in volume. Headwater catchment slopes (mean) are low in Regions 1, 2, and 3 (1.2, 1.8, and 1.3 degrees) and steeper on average in Regions 4, 5, and 6 (2.9, 2.9, and 3.9 degrees). Vegetation characteristics in Regions 1 and 2 are dominated by fens and upland, with lesser amounts of bog. Region 3 has more bog and upland in its catchments. Regions 4, 5, and 6 tend to be either bog (R5) or upland dominated (R4 and R5). Regions 5 and 6 have discontinuous permafrost present in their catchments, and Region 6 catchments have the thinnest soils and most exposed bedrock of all regions.

Water-yields and critical load estimates using the IMB and the WSC methods are compared at lake sites in Figs. 3.2 and 3.3. The results as shown in these figures produce characteristic trends because the SSWC model and the IMB model share all parameters except W_Y. Water-yields determined by the WSC method occurred within a narrower scope and were less variable than the ranges predicted by IMB (Fig. 3.2). The WSC approach approximates the hydrology (water-yields) of lake systems with reasonable output values for W_Y, despite the fact that it is derived from runoff data collected at parent nodes up to 150 km (measured as a maximum of distance downstream length to closest node) away from the sub-watersheds. In general, at systems below water-yields of 100 mm, the WSC method produced catchment water-yield comparatively higher than the IMB model, while in systems with water-yields above 100 mm the WSC method produced lower catchment water-yield.

Comparison of the two results lends valuable insight on system variability. The IMB model is considered to approximate critical loading to the systems with greater accuracy than the WSC method, as the IMB captures greater variation in water-yield, especially at small and large systems in the data set. The IMB model, based solely on three annual water samples, performs notably well, given the relatively short collection period, and without adjustments normally required for water balance measures (see Winter 1981). The WSC method, while it performs reasonably for water-yields, is not robust at the application of critical loading values, as it fails to provide accurate enough variability in estimates and sensitive approximations at the low and high ends of the hydrologic spectrum.

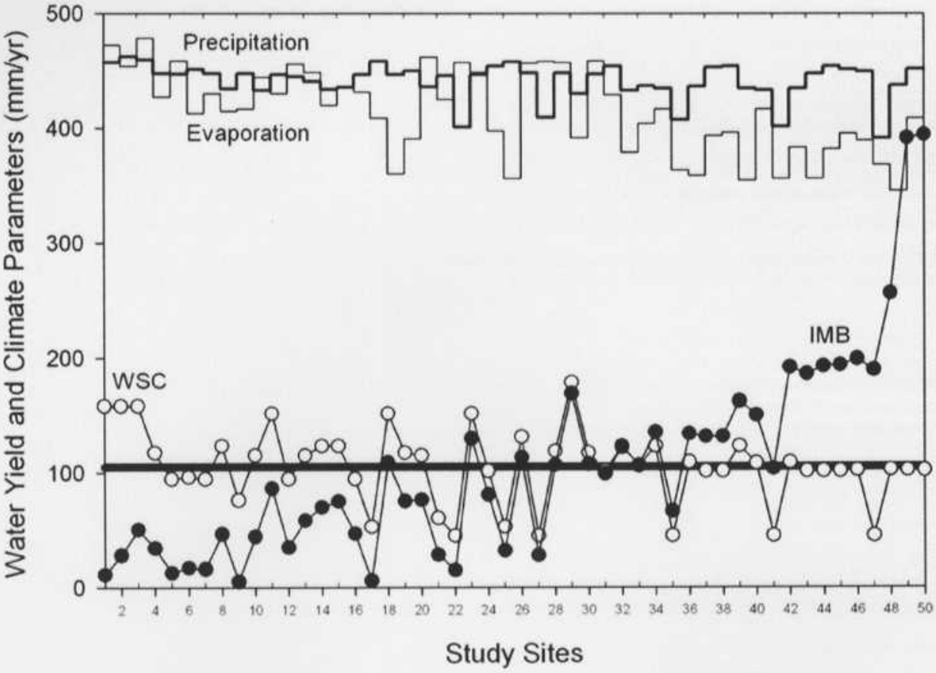

Figure 3.2 Pulse diagram illustrating water-yields and climate parameters. Results are sorted by differences between the two estimates of water-yield (IMB - WSC), beginning with the most negative values (IMB - WSC < 0) and progressing through to positive values (IMB - WSC > 0). Closed circles represent the IMB water-yield and open circles represent the WSC water-yield. Precipitation is shown as a thick black line, evaporation is a thin line (P-E is negative). These estimates are based on the gridded climate analysis and data sources are quoted in Chapter 1. The parallel line illustrates average values for both the IMB method the WSC method (average are similar and plot close together).

The two methods are compared via communality, which is subjectively defined from visual comparison of the two data lines (Fig. 3.3) as the difference between the critical loading assessments of +/-0.10 keq H+/ha/yr and which is referred to in Fig. 3.3 as 'Good agreement'. Compared to the IMB model, the WSC method generates higher critical loads for 33% of the data set, and lower critical loads for 20%. Forty-seven percent of the lakes' critical loads for WSC and IMB are in general agreement.

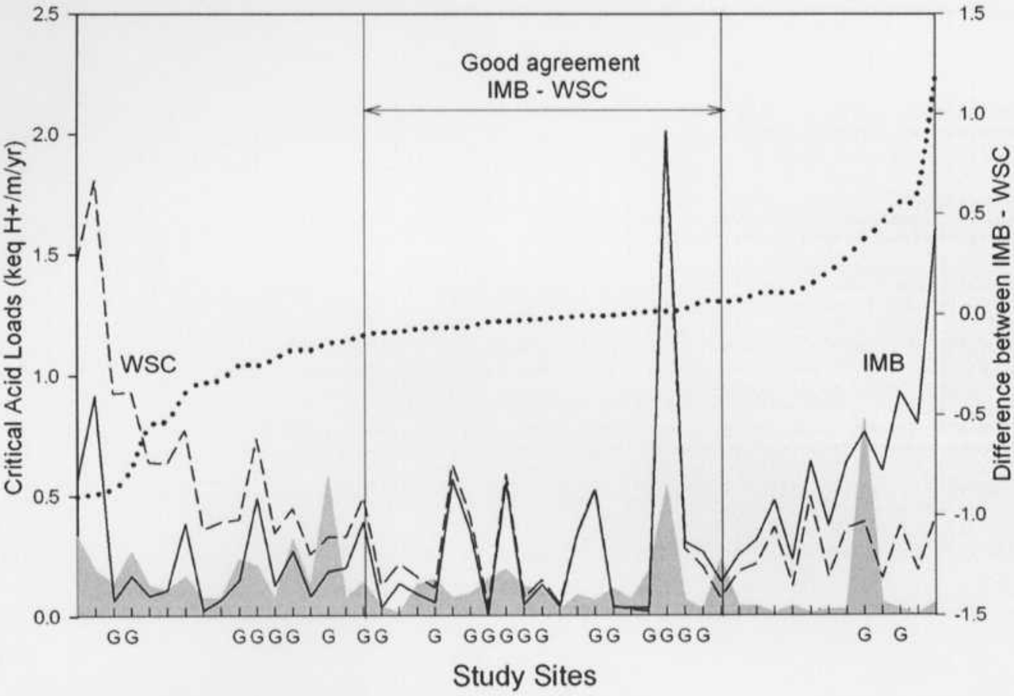

Figure 3.3 Pulse diagram illustrating critical loads of acidity for study sites. The dotted line illustrates the WSC method, the solid line is IMB method. The solid gray background is the PAI value for each study site. When the PAI value is greater than the critical load, sites are considered acid-sensitive. Good agreement (IMB-WSC) is shown where estimates are within +/-0.10 (keq H+/m/yr). The difference between the IMB and the WSC CL_A is given on the right-hand axis. Sites within this range that have an applicable WSC gauge draining them at a downstream node are illustrated with a G on the x-axis. Forty-one percent of all sites are gauged, while 48% of the sites within +/-0.10 (keq H+/m/yr) are gauged and 35% of the sites outside +/-0.10 (keq H+/m/yr) are gauged. Average distance to gauges from headwater lake sites is 87km, with average distance within the +/-0.10 (keq H+/m/yr) data set being 94km.

To understand why some WSC-generated water-yields were similar to the IMB model results, the lakes that fell within the range of +/-0.10 were examined and contrasted with the lake population that fell outside of this range. The lakes within the range tended to be of moderate size and depth, contained no extreme values (i.e. data set minimums and maximums) and in general occupied a middle-of-the-road setting in terms of physical catchment features. The lake systems also had steeper slopes, higher throughflow and shorter water residence times.

Simple regressions were performed between the smaller catchments that comprised the IMB model and the larger, broad-scale catchments drained by the WSC gauges. Drainage basin area, catchment elevation (max, mean, min), slope (max, mean, min), E/I ratio, residence time, stream order, drainage ratio, and vegetation characteristics such as percent coverage of fen, bog, and upland were compared at the IMB catchments and for the WSC catchments, where data permitted. This analysis revealed positive relationships between drainage ratios for the small and large catchments in the matched data set, which were differentiated between DR > 1 ($r^2 = 0.36$, $p = 0.09$, $n = 9$) and DR < 1 ($r^2 = 0.34$, $p = 0.13$, $n = 8$) for WSC watersheds. Drainage ratios in the non-matched data set display a negative relationship for DR > 1 ($r^2 = 0.42$, $p < 0.05$, $n = 10$), and no relationship exists for DR < 1. Slope factors (max, degrees) in the sub- and WSC watersheds are related ($r^2 = 0.42$, $p = 0.06$ $n = 9$) for the matched data set. IMB-watershed slope (mean, degrees, in matched) and WSC watershed elevation (max, meters) were also correlated ($r^2 = 0.60$, $p < 0.05$, $n = 9$). Analysis from the lake population that fell outside of the range of agreement resulted in a negative relationship for slope ($r^2 = 0.21$, $p = 0.11$, $n = 14$), and no relationship was found between slope and WSC watershed elevation.

Further study of the data set based on absolute difference between the IMB model and the WSC method (IMB – WSC) for CL_A at each lake site revealed relationships between what is referred to here as the replication factor of the WSC method and the characteristics of the IMB watersheds. The analysis population was comprised of 45 lakes (the four largest lakes by water-yield were removed), unless otherwise stated. Minimum catchment elevation ($r^2 = 0.10$, $p < 0.05$, $n = 40$) is correlated negatively with the replication factor, suggesting that replication increases at higher minimum catchment elevations. Residence time ($r^2 = 0.44$, $p << 0.01$) and critical loads ($r^2 = 0.26$, $p << 0.01$) are positively correlated: with increasing residence time and critical loads, it is harder to replicate the IMB model. Water-yield and E/I ratios were related to replication, water-yields were negatively correlated with the replication factor ($r^2 = 0.17$, $p < 0.01$), and E/I ratios were positively correlated ($r^2 = 0.19$, $p < 0.01$), suggesting that low water-yields and evaporative lake systems were harder to replicate.

Relationships found in the WSC catchments (WSC) were also investigated based on the replication factor. It is easier to predict the IMB model when WSC catchments have steeper mean slopes ($r^2 = 0.12$, $p < 0.05$, $n = 38$) and more fens (based on the sum of fen area, $r^2 = 0.12$, $p < 0.05$, $n = 40$). Bogs (% in catchment) are positively correlated with the replication factor ($r^2 = 0.11$, $p < 0.05$, $n = 40$): it is more difficult for the WSC method to replicate the IMB model in watersheds with larger amounts of bog.

Exceedance measures based on the IMB W_Y estimates indicate that 17 systems are exceeded in the regional area, and average values for the exceeded and the non-exceeded populations. No lake systems in either the Caribou (R5) or Shield (R6) lake areas were exceeded. Most of the exceeded lakes are located in the Stony Mountains or West Fort McMurray. Table 3.3 lists the general features for these lake systems by regional area. All lakes are smaller than 1km^2 with the exception of the lakes found within the Stony Mountains. The Birch Mountain catchments (DBA) are almost ninefold lower than the non-exceeded average. DR and NCA/LVOL are twofold the non-exceeded average, again with the exception of the Stony Mountain sites. Thus, these sites represent, on average, the smaller lake/catchments receiving the influence of greater drainage from their catchments in comparison to their volume/size (higher NCA/LVOL, and DR). Lakes are also more evaporative, have lower water-yields, and residence time is shorter in these systems as compared to the non-exceeded average.

Table 3.3 Exceeded systems and their physical, hydrologic and chemical properties for each region area. Data set averages for both exceeded and not exceeded populations are given. Exceeded lakes is the count of lakes from each region where the potential acidifying input is exceeding the critical load, Area = lake surface area, DBA = drainage basin area, NCA/LVOL = net catchment area over lake volume, DR = drainage ratio, Wet% = percentage of catchment wetlands, Wy = water-yield, τ = residence time (days).

Region	Exceeded Lakes (#)	Area (km^2)	DBA (km^2)	NCA/ LVOL	DR	Wet (%)	E/I (%)	W_Y (mm)	τ (days)
1	3	0.3	10	39	40	74	16	79	85
2	6	1.3	15	17	12	67	44	70	139
3	6	0.9	18	33	30	66	57	17	200
4	2	0.4	5	65	20	24	28	107	43
Average Exceeded	**17**	**0.9**	**14**	**32**	**24**	**62**	**42**	**58**	**140**
Average Not Exceeded	**23**	**4.5**	**30**	**15**	**14**	**40**	**35**	**128**	**210**

The critical acid loading model was analysed for uncertainty, with special regard to the differences between the chemistry (base cations, BC, and the acid neutralizing capacity or ANC limit) and the hydrologic estimations. The key conclusion from this analysis is that all hydrologic variables are more sensitive than the variants of chemistry estimations, BC, and ANC.

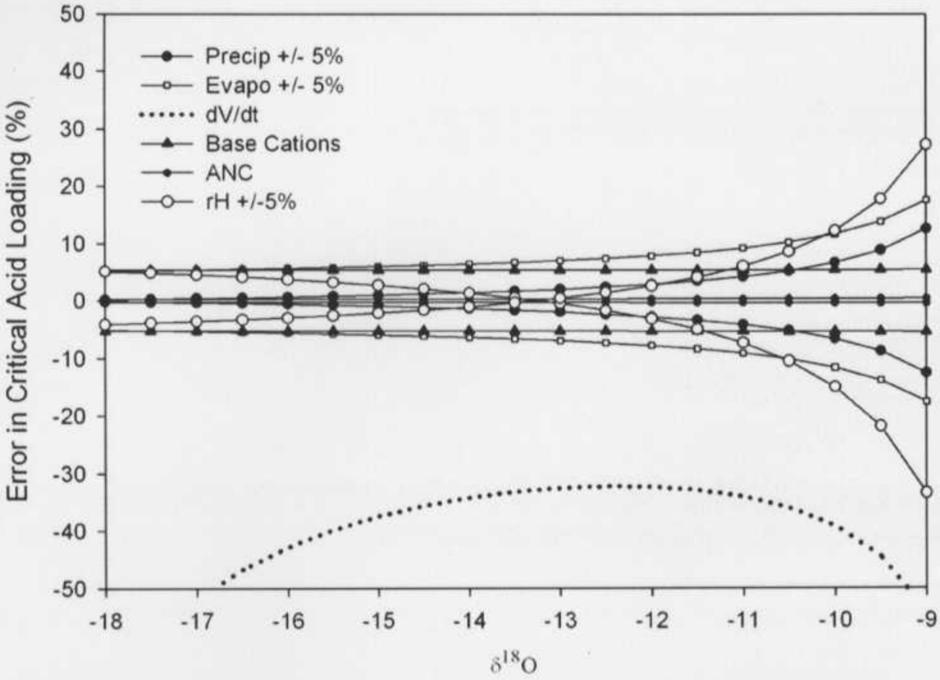

Figure 3.4 Sensitivity analysis illustrating error in critical acid loading. Variables are listed in order of most to least sensitive: volumetric reservoir drawdown (dotted line), relative humidity (open circles on a solid line), evaporation (open squares on a solid line), and precipitation (closed circles on a solid line), base cations (closed triangles on solid line), and the ANC limit (hexagon on a solid line).

V. Discussion

This study applies the use of a stable isotope mass-balance model to calculate water-yield and critical acid loadings for northeastern Alberta's Boreal Forest lake systems and compares these results with a WSC-based approach to water-yield and acid loading estimation. The strength of the WSC method is temporal robustness, in that it relies on long term monitoring, whereas the strength of the IMB method is spatial robustness, in that it provides lake-specific estimates. Stable-water isotope tracers can be collected during routine chemistry sampling and therefore provide an economically-feasible option to instrument-intensive monitoring or long-term gauging at these remote sites. The IMB method is remarkable in that it provides accurate water-yield estimates within a comparatively short period of study (3 years in this application) and performs well in the middle and at both upper and lower ends of the hydrologic spectrum. It is apparent that gauged basins, despite years of monitoring, may never capture the scale-related hydrologic variability present within landscapes. Sensitivity analysis shows that water-yields (in the IMB model) measurement is a sensitive parameter in the critical loadings analysis, over both base cation and ANC measurements. Thus the accurate estimation of water-yield is very important in order to properly assess critical acid loadings in this landscape.

The IMB and WSC methods each provide different assessments of the hydrology of the systems (Fig. 3.2), which evidently has an impact on the resulting estimates of CL_A (Fig. 3.3). Observations of the landscape and lake morphometry alone suggest that a variety of hydrologic conditions are represented within the data set. The IMB model derives E/I ratios to calculate lake hydrology independent of catchment characteristics and to provide a range of evaporative conditions for the surveyed lakes. E/I ratios reflect a wide variation in water-yields from regional study zones, and high E/I values are indicative of low water-yield areas, such as those found in Region 3.

The hydrologic conditions observed at study lakes are directly comparable to previous studies in the region (Environment Canada 1978, Gibson *et al.* 2002, Prepas *et al.* 2001, Ferone and Devito 2004) and indicate that the WSC method does not provide similar ranges of water-yield or drainage ratios, especially for low-flow sites such as ponds. The WSC method falls short in some of the most sensitive systems, such as the small, evaporative ponds (38% of the systems where IMB W_Y is less than 100 $mm \cdot yr^{-1}$ are exceeded, while none of the systems with water-yields above 100 $mm \cdot yr^{-1}$ are exceeded). Combined use of these two approaches may improve confidence in the overall assessments, and could be helpful in establishing subsets of lakes that are suitable for extrapolation using the longer-term hydrometric records. However, the IMB method clearly offers a more accurate assessment of the hydrology over the WSC method, and provides representative estimates for water-yield that span a range of conditions on which to base further analysis and research, such as critical loading estimates.

Figures 3.2 and 3.3 show the results of water-yields and critical loading analysis organized by percentage difference between the IMB and the WSC methods. Fig. 3.2 illustrates how water-yields may be over-represented by the WSC calculations for small, shallow systems, while the large, deep lakes tend to be under-represented by the WSC method relative to the IMB method. Four lakes that were found to have high water-yields are situated in the Caribou and Birch Mountains, zones of enhanced regional groundwater flow, and may reflect deep regional groundwater inputs occurring outside topographically-defined local catchments (Toth 1963).

Generally, the WSC method best represents the average-sized systems. Lake volume, max depth, drainage basin area, water-yields, and slopes are all of moderate size compared to the lake populations below and above the +/-0.10 keq H^+/m/yr threshold. The lake populations can be divided into three subsets: the over-predicted small lakes (-0.10 keq H^+/m/yr), the mid-sized systems, and the under-predicted large systems (+0.10 keq H^+/m/yr). Small lakes, small drainage basins, low volumes, low angled slopes and lower percentages of upland in catchments are characteristics of the over-predicted systems. In these small catchments, evaporation (E/I ratios are highest) is the dominant process, which makes prediction of water-yields and subsequent CL_A estimates challenging.

On the other hand, under-predicted systems with larger drainage basins, steeper slopes, and greater percentages of upland may also be difficult to predict. Steeper slopes are indicative of upland areas that are less likely to be connected to the watershed as a whole (Dillon *et al.* 1991). Less steep slopes, on the other hand, are common features of wetland areas or ephemeral draws that are more likely to support hydrologic connection to lake and outlets (Dillon and Molot 1997, D'Arcy and Carignan 1997, Dillon *et al.* 1991, Halsey *et al.* 1997). In this study, larger drainage basin areas and percentage of upland may be difficult to predict, owing to greater complexity of landscape found within larger catchments (Clair *et al.* 1994) and the variation inherent in watersheds of greater extent (Prepas *et al.* 2001). Understanding these relationships and the link between landscape and variability in runoff can be useful in scaling down WSC water-yield estimates to the headwater or to a smaller-scale drainage basin level.

The two methods appear to be in agreement where broad-scale and small-scale study basins exhibit a positive relationship between mean drainage ratios, slopes and elevations. This simple finding underlines the importance of commonality in drainage ratios (Steedman 2000, Scully *et al.* 2000) and the significance of slope and elevation in controlling runoff depths in the area (D'Arcy and Carignan 1997). The relationship for slope and elevation in the replicated cases suggests that positively increasing slopes and slopes and elevations in both small and large catchments may assist in better prediction using the WSC method. The negative relationship for slopes and the lack of relationship between slopes and elevations in the non-matched data sets indicate that when these factors are not positively correlated, it may be difficult to accurately apply a regional runoff coefficient to estimate water-yields and perform CL_A analysis.

Replication was enhanced when elevation and slopes were higher, water-yields were greater, evaporation (E/I ratio) was low, and residence time was lower. The Boreal Plain in general is characterized by a net water deficit (Winter, 1989, Ferone and Devito 2004), i.e. evaporation generally exceeds precipitation, so that lakes depend on runoff from the catchment or groundwater inputs to maintain a long-term hydrologic balance. This segment of the analysis suggests that in some catchments high elevations, steeper slopes and more upland may promote higher water-yields and greater runoff contributions to lake systems, enhancing throughflow.

On the other hand, processes occurring within the low-slope catchments also affect water-yield using different mechanisms. Wetland-dominated headwater catchments are a common feature in this landscape (Vitt *et al.* 1996) and greatly influence hydrologic processes in this region (Gibson *et al.* 2002, Prepas *et al.* 2001). In this respect, fens in northern Alberta are known to be more effective in conveying water from the catchment to lakes, whereas bogs tend to be less effective (Halsey *et al.* 1997, McEachern *et al.* 2000). In the current study, headwater catchments where IMB and WSC CL_A results were found to be similar also tended to have higher slopes (and possibly less wetlands) increasing with closer agreement between WSC and IMB estimates. Fens were more common features of the matched lake population, which indicates that increased amounts of fen in these systems may be contributing to ease of replication. Greater fen percentages may account in part for this ease of replication, due to enhanced connection of these systems to uplands and other saturated areas, such that they function as runoff conduits within this landscape. Fens potentially support better defined drainage, while bogs may contribute to retention of water in the catchment and water-yields.

The percentage of gauged systems that fall within +/-0.10 for the two estimates of CL_A is higher than those outside this range, indicating the importance of density within a hydrometric station network. In locations where hydrometric station density is low, estimates for water-yield may not reflect the regional character for smaller-scale basins. Within the +/-0.10 range, results do not improve given decreased distance to the gauge, which suggests that it may not be the gauge distance so much as the landscape characteristics and linkages between the IMB and WSC watersheds that play a role in improved prediction. However, these results indicate the significance of having representative hydrometric networks monitoring a variety of streams across representative and diverse landscapes, and the importance of continuous gauging throughout summer and fall periods to capture the widest variation in hydrologic regime possible. Hydrometric gauging data used in this study was based almost wholly (82%) on seasonal monitoring sites, and of the continuous monitoring sites, all have since been discontinued.

Regions 1 and 2 show the best agreement between the approaches for water-yield and critical loadings assessments. These areas have relatively high numbers of gauges monitoring their downstream nodes (82% and 40%, respectively). Region 1, which has the most gauges, accurately reflects the hydrologic state of the IMB drainage basins, even though they are located downstream of the headwater study systems. Sandy soils common to the area (Abboud *et al.* 2002) may also play a role in promoting drainage. Slopes are also shallower (1.5% on average) in these regions, and are reflective of average slopes for the broad-scale catchments found in this region. Shallow slopes are also indicative of greater amounts of peatland and, in particular, fens, which are correlated with higher water-yields in the matched data set. The matched basins in Region 1 also have more fens over other regions, which, as discussed, can promote flow in some cases via increased hydrologic connectivity and surface saturation processes.

Region 3 shows moderate agreement between the Wy estimates for the two methods but shows the greatest difference in critical loading estimates. The watersheds in Region 3 have fewer gauges monitoring their WSC watersheds than do catchments in Regions 1 and 2. In Region 3 the predominance of small, shallow lakes with large drainage ratios is a likely cause of the lack of agreement between the W_Y results and hence, CL_A results.

All of the small ponds in Region 3 have higher CL_A values by the WSC method compared to the IMB method. The one system in Region 3 that falls within the +/-0.10 range is a medium-sized lake with a drainage basin of average size. Region 3 also contains mostly bogs and uplands, and has lower average mean slopes. The bogs may be retaining water (Halsey *et al.* 1997), while the uplands may be disconnected from the lakes, contributing to low water-yields and challenging predictive ability of the WSC method. These small, shallow lake systems are also found within larger DBAs, which lend greater uncertainty to prediction of water-yield and CL_A. These systems are also the most evaporative out of all the regions, another confounding factor in replication.

Regions 4 and 5 show poor agreement between W_Y calculations, and Region 6 shows moderate agreement for W_Y but poor CL_A agreement. This is likely because of the lack of WSC gauges in these regions, and the large, deep lakes common to these regions. These more northerly, higher (elevation) regions may experience high flows in spring freshet and low winter and summer flows, extremes that are not well represented by the WSC gauged sites (Environment Canada WSC 2002, Winter 1989). Steeper slopes may promote higher water-yields, but in these cases of Regions 4 and 5, large watersheds, bogs, and permafrost may complicate the hydrologic picture. Regions 4 and 6 are predominantly uplands, while Region 5 has many bogs and, as well, permafrost is prevalent, complicating the runoff regimes from steeper slopes and potentially preventing vertical recharge. Runoff that may occur in Region 5 from steep, frozen soils is possibly retained in the bogs once the flow reaches the valley bottoms. Region 6 catchments have steeper slopes, thin soils, and are throughflow systems, which are generally best represented by the WSC method, but critical acid loading is erroneous, perhaps due to the longer water residence times found within the large, deep systems of this region.

VI. Implications and Future Directions

Exceedance is a measure of the sensitivity of a lake system based on the critical load analysis and the potential acidifying input for the lake basin. Initial estimates based on hydrometric data suggested that 10 of 49 lakes surveyed in northeastern Alberta were acid-sensitive. Revised estimates based on this study calculate an additional 7 lakes are potentially acid-sensitive, which illustrates the importance of the hydrologic parameter in critical loadings assessments. Although water-yield estimates from the two approaches on average may be similar, even small discrepancies start to affect performance once the CL_A analysis is applied. In this case, CL_A is evaluated on the basis of exceedance, and the changes that are a consequence of the IMB application produces a 20% to 35% increase in exceedance, and an overall 39% change in these estimates. As changes to the lake data sets are non-linear, there is no means to correct or adjust the WSC water-yields estimates, therefore systems must be re-evaluated individually to determine whether the WSC estimates are accurate.

Seventeen systems exhibit acid-sensitivity based on exceedance of the potential acidifying input (PAI, WRS 2004). Systems in the Birch Mountains (2) that are exceeded were both small, deep lakes with small catchments, experiencing high water-yields and low water residence time. Here, high delivery of humic substances from the catchments could be leading to acidic conditions at these lakes. In the NE, lakes are likewise experiencing higher water-yield and faster flushing. Thus, the acidic conditions of the soils in combination with high percentages of bogs and fens may be delivering high levels of acidic humic waters to the lakes in this region. Overall, acid-sensitive systems were lower in these regions as compared to the Stony Mountains and West Fort McMurray sites. This could be owing to the deep, groundwater-fed lakes found in the Birch Mountains, which may be buffering acid contributions to lakes in this region.

In the lowland region of West Fort McMurray, lakes appear buffered but evaporative conditions and high percentages of peatland and in particular, fens in catchments could be affecting the acid status. More research is necessary to understand the conditions occurring at these lakes systems; in-lake generation of acids could also be occurring owing to the high levels of aquatic vegetation and very small, shallow systems found in this region.

The Stony Mountains have moderate water residence time, low deciduous forest cover within their catchments, and lower water-yields. Lakes are large in surface area in comparison to catchment, thus they are evaporating at higher levels. Acid generation may be occurring due to the humic levels of input waters that are then degrading in-lake to form strong acids and/or concentrating in some form. The lack of buffering owing to sandy, eolian deposits in uplands, drainage basin morphology (lake area/lake volume to catchment area ratios), low deciduous forest cover, lake of groundwater connections to provide buffering inputs and non-permafrost bogs exacerbates the conditions in the Stony Mountains. Although the exact processes remain unclear, the Stony Mountain lake sites should be carefully monitored to ensure further acidification is not occurring and to determine the true impact of humic acids on these lakes in the context of the critical acid loading model.

The accuracy of the water-yield calculation impacts the CL_A results, which then has an affect on the exceedance estimates, which are the base for emissions release standards for oil sands companies and other industry. This type of study has never before been undertaken in northeastern Alberta, and it is therefore considered to be the baseline for this region. This baseline information is vital as it will be used to evaluate future shifts in critical acid loadings to aquatic ecosystems based on increased output from oil sands development. The findings, as presented in this thesis chapter, point to the need to refocus management concerns on designing sustainable thresholds for acid loadings in the region and elsewhere using the best available methods.

This study has demonstrated the added value in use of an isotopic approach for predicting water-yield in ungauged lake basins. Evidently, regionalization of water-yield data from conventional hydrometric gauges should be used with caution, due to scale-dependent water balance variability. Critical acid loading analysis is particularly sensitive to the hydrological parameter, given the structure of the CL_A equation. Such analyses would clearly benefit from the additional spatial robustness provided by site-specific isotope tracing, and may help to identify causal factors controlling variability among spatial scales.

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Conclusions

Chapter 1: The stable isotope mass-balance method: toward improved models for assessing regional hydrological variability on the Boreal Plain

An isotope mass-balance approach to understanding catchment and lake hydrology was applied in the Boreal Forest region of NE Alberta. This model was successful in applying a first approximation of throughflow, water-yields, and residence times for lakes sites. Success was measured in this case through replication of the isotopes signal in lake water and tracing of evaporative flux over the seasonal (four months) and the annual (three years) periods of the sampling routine. Measurement of system end members, namely the isotopes in precipitation, shallow and deep groundwater sources, and local runoff (rivers) further substantiated the isotope mass-balance model to the expected, theoretical structure. Field observation, analysis of landscape and comparisons to previous work also indicate that the wide variation in hydrologic signal as measured by the isotope model is indicative of the water balance conditions found within this region. This tool is particularly powerful as it can be implemented into routine monitoring schedules; therefore it is ideal for use in this remote and expansive terrain. Furthermore, its cost is none to alternate water balance techniques, which require expensive and time-consuming instrumentation, monitoring and also present associated inaccuracies and validation challenges.

Testing and analysis of model frameworks, output and sensitivity allowed for understanding of the isotope mass-balance model limitations. As such, one approach (amount-weighting of isotopes in precipitation) was found to be overly sensitive and thus was not applied in the final version of the isotope mass-balance model. At the throughflow end of the hydrologic spectrum at low levels of isotopic enrichment, isotopes in precipitation were found to be sensitive up to 30%. Relative humidity was the most sensitive of the input climate variables, and is sensitive at high levels of enrichment at the evaporative end of the scale on the order of 15%. This finding should be carefully considered, as the selection and application of estimates for relative humidity may affect the isotopic model output values.

Gridded climate models were used in this application, and are inherently flawed in that they are generally developed from point-based estimates (climate stations), which are then interpolated to grids. This analysis has also added an additional measure of uncertainty by downscaling the gridded products to allow for interpolation at lake sites. However, this region had neither the topographic range present to cause great anomalies (for example, as found in British Columbia's Rocky Mountains) nor does the isotope mass-balance model use extreme climate values in its application (as values are weighted by evaporation, data are focused to the open-water season months only). Although more detailed information is preferable, in the absence of any information, the gridded climate data provided an estimate of the climate variables and allowed for a first approximation of water budgets at lake sites.

Year-to-year variation in water budgets varies in this region based on prevailing weather patterns and antecedent moisture conditions. These differences are not possible to observe in the isotope mass-balance model given the application of 30-year climate estimates for climate parameters. However, the year-to-year variations (based on analysis at the Fort McMurray climate station) for the duration of the research as compared to the 30-year average were significantly different during 2002 (snowfall) and 2004 (temperature) study years. Although these variations did occur, it is not anticipated that they will affect the isotope mass-balance estimates because of the averaging methods and sampling protocol applied in the modelling approach. The isotope mass-balance estimation, however is best relied upon at the long-term average time scale and is not appropriate for use to estimate dynamic variability in hydrology at this point in time.

Hydrologic throughflow, water-yield and residence time differed at the lake sites and was reflective of differences in lake size, drainage basin area, volume, and drainage ratios. The data set was skewed towards the upper end of the hydrologic spectrum, and this feature can be traced through parameters of lake size, drainage ratio and the hydrologic estimate for throughflow (E/I). High throughflow, high water-yield lakes tend to be located in the north and evaporative, low water-yield lakes were found in the south. Lake areas were greater for evaporative lakes versus throughflow systems, indicating that these lakes undergo the highest levels of evaporation owing to the extent of their surface area.

Chapter 2: Regional hydrologic, physical and chemical interactions of Boreal Plains lakes systems, NE Alberta, Canada

Water-yields in catchment systems varied greatly, reflecting the trends outlined in Chapter 1 for E/I ratios. High water-yields were found in the upland regions while low-water-yields were most prevalent in the lowland, wetland-dominated regions. Water-yield was not directly related to E/I ratios because of variations unique to lakes and their watersheds, patterns that could also be observed to be occurring at the scale of the regional study areas. Water-yields were significantly affected by the slope and drainage ratio across all study sites. However, when low water-yield and high water-yield data populations were considered, it was clear that low water-yield sites (with more wetlands) were impacted by alterations in drainage ratios and slopes. The high water-yield sites tended to be driven predominantly by their lake basin size. This finding suggests that low water-yield catchments will respond to shifts in slope and drainage basin contributions, thus may be more affected by hydrologic transfer through their catchments, even if the specific amounts are low. This effect may also be a result of differing conditions at high and low water-yield lakes in this study: such as groundwater contributions, permafrost/soil freezing, surficial geology and cover types (forest, wetlands).

Lake water chemistry was highly variable across study lakes, differences could be traced to high and low water-yield mechanisms. Major ions and conductivity differences at lake sites could be largely explained by groundwater influence occurring at lower elevations, lowland sites had higher values likely owing to increase interaction between wetland coverage and groundwater. pH values were lowest at the Stony Mountains, where groundwater and non-permafrost bogs do not provide buffer from acidic inputs of DOC. At these sites, weak organic acid may be degrading owing to longer water residency, and/or strong acids are concentrating owing to the evaporative nature of the large lake surface areas and relatively low catchment drainage area ratios. Colour was lower at the Stony Mountains, which also supports the conclusion that weak acids are being broken down by some mechanism in these systems.

The percentage and type of cover in the catchments appeared to influence water chemistry. At lowland sites, deciduous forests in uplands zones of catchments appear to be affecting DOC and colour. This suggests that in some systems, forest cover types in the upland areas is affecting water in the lakes, even in the cases where water-yield is very low. Fens appear to be most commonly adjacent to deciduous uplands in the lowland, low water-yield sites, which suggests that they are effectively translating water to the lake system and its related constituents. These effects could be spurious, as lowland, deciduous sites also likely are connected to groundwater tables, which could also be affecting water chemistry.

Nutrients were very high in these systems, and in particular, within the lowland catchments of West Fort McMurray. These small, evaporative ponds with high inputs from wetlands and deciduous forest cover appear to export nitrogen whereas deeper lakes appeared to degrade nitrogen. Phosphorus, on the other hand, was higher in the upland locations that had permafrost features in their catchments and prevalence of bogs. Fens were found to sequester phosphorus, concurrent with other research findings in this region.

Chapter 3: Refining estimates of water-yield for critical loadings assessment: an isotopic approach

Chapter 3 presents the results of comparative analysis of water-yields and critical loadings assessments using a) the WSC catchment method and b) the isotope mass-balance model. The isotope mass-balance model is able to estimate a range in water-yields as reflected by the landscape and in other studies, whereas the WSC catchment estimate falls short in the low end of the hydrologic spectrum. It appears that the WSC approach is best suited to moderate systems that have moderately sized lakes, small drainage basins and low amounts of wetland cover. Large drainage basins and/or high wetland cover tend to complicate hydrologic functioning of the catchments and therefore may make it difficult to apply broad-scale methods of assessing water-yield.

The importance of communality between drainage basins used to estimate runoff was proven in this chapter. Water-yields based on WSC runoff estimates were closer in approximation to the isotope mass-balance water-yield derivations in the cases where the large and small catchments had similar drainage basin and slopes. This simple finding indicated that results are meaningful only when factors are common between the large-scale drainage basins and the basins to which the water-yield application is being derived.

Replication by the WSC method was clearly influenced by catchment parameters such as the type and occurrence of wetlands, and high or low water-yield. Watersheds with greater percentages of fens in particular, could be assessed by the WSC estimation, therefore fens in this study area may be acting as conduits to transfer water across the landscape. Bogs, on the other hand, may have more complex mechanisms of water storage and delivery, owing perhaps to the association of bogs in this region with upland permafrost distribution.

The capacity to estimate water-yields from estimates based on regional runoff values derived from the hydrometric gauging network is in part dependant on the density of this network. A greater percentage of gauged systems could be accurately assessed by the WSC technique, which indicates that improved estimates could be obtained with a more highly populated drainage network. In this region, multi-stakeholder groups are facilitating installation and monitoring of additional stream flow stations, which will become a valuable tool to augment the existing Water Survey of Canada gauging system.

Acid sensitive systems in this study are determined based on exceedance. Exceedance occurs when the potential acidifying input factor is greater than the critical acid load and is lake specific. Seventeen lakes were deemed acid sensitive based on the revised estimate for critical acid loadings. This is almost two-fold the estimate based on the hydrometric gauging runoff estimates. Most of the systems that were found to be acidic were located in the upland Stony Mountains and the lowlands of West Fort McMurray. A high percentage of bogs and/or conifer forests, and low buffering input from groundwater inflows were characteristics of these sites. Four exceeded lakes in West Fort McMurray had high amounts of aquatic vegetation, which may be affecting these systems, lending to in-lake generation of acidifying chemistry. Fens were a dominant feature of the landscape at the remaining acid sensitive sites, these fens could be contributing acid humic inputs to lake systems.

The Birch Mountain sites that were sensitive were small and fen-dominated. Likewise sensitive NE Fort McMurray systems were small, had large catchment to lake volume ratios, and had a very high percentage of wetland coverage. Both regions experienced higher water-yields. Thus, these systems were probably receiving very high contributions of concentrated acid humic waters to their lakes via the hydrologic cycle. However, buffering by groundwater contributions occurred in these regions and led to a low sensitivity of lake systems. Three systems in West Fort McMurray of moderate size were highly evaporative and had low water-yield, likely they are also receiving high amounts of acid humic waters that were then concentrating in the lakes.

The Stony Mountain upland systems were unique in their acid sensitivity. These systems are larger and have low drainage ratios. Buffering is low at these sites owing to highly sandy silt soil matrices, the predominance of upland conifer vegetation, and a lack of groundwater inputs. Here as well, wetlands contribute high amounts of humic waters, which are delivered by the moderate water-yields, evidenced by the higher than average DOC concentrations in these systems. However, in these lakes sites, colour is slightly lower, which suggests that weak, protective acids are being broken down by moderately long water residence time.

In Summary

This study has undertaken a first approximation of water balance in 50 lakes using an isotope mass-balance approach. This approach applied rigorous methods to determine the best available data and to ensure that the data in context of the isotope mass-balance model structure was robust. The results of this initial body of work (Chapter 1) was then used to document, discuss and evaluate relationships between hydrology, landscape and lake water chemistry to determine the spatial location of sensitive systems and understand relationships between water-yield, catchment characteristics and water chemistry (Chapter 2). Finally, the results of the water balance analysis were compared and contrasted with an alternate approach to estimating water-yields (Chapter 3). Critical acid loadings were generated and these results were then investigated and contrasted with the results from the previous assessment.

The objectives of this research were primarily to assess the isotopic mass-balance approach to determine if it was applicable in this landscape. Following this, the sections detailing relationships between hydrology, landscape and chemistry and assessment of critical acid loading demonstrated the use of an isotopic mass-balance method for analysis of acid-sensitive systems on the Boreal Plain. Although results have provided valuable insight into the hydrologic function of the lake systems, a note of caution accompanies this first approximation: continued development to fine-tune this work and system end members using detailed, site-level information may alter relationships or thesis statements.

The intention is to submit versions of the enclosed chapters for publication in peer-reviewed scientific journals. Chapter 1, due to its length, will be divided into a two-part manuscript, with the first part focussing on the comparison of the performance/realism of the three basic isotope mass-balance models, and the second part focussing on the fine-tuning of field-based strategies for improving the definition of model end-members in general.

Recommendations

Logistical Recommendations

1. Apply the flux-weighting techniques at a daily level to test improved capability of the flux-weighting procedure.

2. Run the model for the three years of data collection (2002-2004) to determine variations based on year-to-year weather patterns.

3. Develop the isotope estimates relative specific to each region to determine the change to the model output.

4. Detailed, low-level surficial geology and wetland mapping should be undertaken at all 50 lake sites. Soils data should be extended to cover the Stony Mountain plateau. Recent air photography and/or imagery should be captured at the lake sites to update vegetation mapping in this area.

5. Climate data could be compared to station level data available through the newly established monitoring networks that will now have baseline data available for analysis of precipitation and temperature. Relative humidity and evaporation data should be collected for at least two sites in this network, if not more. If this addition has not been addressed, future program additions should consider such instalments to climate stations.

6. Update the IMB critical acid loadings model to incorporate DOC based on the most recent version of the mapping as outlined in the 2005 RAMP report.

Theoretical Recommendations

7. Develop an isotopic database from boreal land surfaces to map the continuum within wetlands (bogs, poor fens and fens), and at hillslope-wetland interfaces and within remnant permafrost features across these study sites. Capturing both isotope and water chemistry will allow for understanding of both hydrologic flow and the water chemistry interactions at specific points in the landscape continuum. This should shed some light on the process and mechanisms of deliver occurring within the lowland and upland locations. Seasonal study should be considered so as to allow for capture of the spring freshet and to understand how soil thaw during freshet periods may be influencing the hydrologic water balance in these catchments.

Appendix A: CLIMATE DATA MANIPULATIONS

Climate Data Extraction and Manipulation Routines

Each of the different climate data sets required extraction and conversion procedures to retrieve the data for each lake site. The following routine described in this section was undertaken for the NetCDF file formats of climate data. This general treatment was applied for data sets prior to manipulation in a GIS and extraction for site-by-site analysis. Section Y describes the specific data extraction and manipulation procedures undertaken for each individual data set.

General Data Extraction and Manipulation Procedure for netCDF Files

Once data sets were downloaded, they were extracted using GRADS; a utility program that allows a user to view, merge, summarize and unpack the netCDF climate data file formats to ASCII data arrays. Data was unpacked to an ascii text file using Unidata's NetCDF 'ncdump' utility[1]. Files were then manipulated using a text editor to separate them into monthly arrays, when necessary. Once mean monthly data arrays were separated, some files required further manipulation, these files were loaded into a Java based imaging package (ImageJ) which will allow export of arrays by X,Y,Z (data value) coordinates.

These files were formatted and loaded into ArcGIS using an import function and converted for display as point data sets. Depending on the data set, further manipulation was required to bring the data set into a common projection; this was done via shifting the X,Y data points appropriately to bring the alignment back to a Geographic Cartesian projection. Data points were shifted from an X, Y linear space to a Cartesian grid with X values ranging from –180 to +180 and Y values from –90 to +90. Once the data points were re-aligned, the data was clipped to a buffered polygon of the province of Alberta. The point data was rasterized using the IDW nearest neighbour grid function component of ESRI's Spatial Analyst to create a standard 20 x 20 metre grid coverage for Alberta. From these data sets, individual values for all lake centroid data points were extracted at each monthly time-step intervals using 3D to 2D overlay extraction routine using the Spatial Analyst's Zonal Statistics feature. All data sets were saved as spreadsheets for further analysis.

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[1] Web site address: www.my.unidata.ucar.edu/content/software/netcdf

Specific Climate Variables and Model Extraction and Manipulation

Evaporation

The Hamon Method

Hamon (1961) developed a relatively simple method for estimating monthly evaporation based on monthly average temperature, number of day light hours in any given month, and saturated vapour pressure (see Haith and Shoemaker 1987), calculated as:

$$(1)\ E = \frac{2.1 H_t^{\,2} e_s}{T_t + 273.2}$$

where

E = evaporation, month t [mm month^{-1}]

H_t = number of daylight hours (average) occurring per day in month t

e_s = saturated vapour pressure at temperature T

T_t = average monthly temperature at month t

Day length (in hours, H_t) can be estimated using the following equation:

$$(2)\ H_t = 2 * a\cos\frac{(-\tan\phi \tan\varpi)}{0.2168}$$

where

ϕ = solar declination of the sun for the month (averaged) in radians

ω = latitude of the site in radians

and e_s or saturated vapour pressure of water in air at temperature T can be calculated as:

$$(3)\ e_S = 0.6108^{\left(\frac{17.27T}{275.3+T}\right)} * \sigma$$

where

$\sigma =$ 2.71828183, conversion from T[kPa] to T[°C]

Three different temperature estimates were used to calculate separate Hamon estimates of evaporation: the CRU 10-degree data set (New *et al.* 2002); the CRU 0.5-degree data set (New *et al.* 1999); and the NCEP temperature data set (Kalnay *et al.* 1996). The

Hamon approach outputs monthly data values for each site; therefore monthly values were summed to arrive at a total annual evaporation estimate for each lake site. For information regarding the extraction of the CRU 10-degree, CRU 0.5-degree and the NCEP data, please see the section outlining temperature data manipulation.

NCEP/NCAR Reanalysis Data

Potential Evaporation Rate (W m^{-1}) is published through the CDC and available in NetCDF format as a monthly long-term global mean surface level flux *(*NCEP Reanalysis data provided by the NOAA-CIRES ESRL/PSD Climate Diagnostics branch, Boulder, Colorado, USA, from their Web site at *http://www.cdc.noaa.gov/* or see *http://www.cdc.noaa.gov/cdc/data.ncep.reanalysis.derived.html,* Kalnay *et al.* 1996*).* This data set is created using the average monthly means from the 1968 to 1996 climatology. The T62 Gaussian grid with 192x94 points grid array was smoothed and re-extracted in a regular grid array using the Java-based tool as described in the first section of this Appendix.

European Centre for Medium-Range Weather Forecasts (ECMWF)

The ECMWF 40-year Reanalysis[2] (Uppala 2001) monthly daily mean (averaged over six-hourly observations) evaporation data was downloaded for the period of 1960 – 1990 in NetCDF format for North America in a 2.5 degree by 2.5 degree (29 x 17) array. The NetCDF file format was unpacked for each monthly file and converted to a text file, re-formated with appropriate header information. The files were then input into ArcGIS as grids, which were re-gridded to the 20m x 20m format to allow for interpolation at each lake site by month.

Thornthwaite Potential and Actual Evapotranspiration

The Thornthwaite water balance model (Thornthwaite 1948), which includes an estimate of potential and actual evapotranspiration as presented by Dingman (2002) was used to calculate both potential and actual evapotranspiration.

Canadian Global Climate Model

The Canadian Global Climate Model (CGCM2, Flato *et al.* 2000, Kim *et al.* 2002) evaporation data were downloaded from the CICS website[3] for the 1961 – 1990 baseline.

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[2] Web site address: www.ecmwf.int/

[3] Web site address: www.cics.uvic.ca/scenarios/data/select.cgi

Several scenarios were downloaded, the Economic Regional Focus Simulation 1 (SRES1), SRES2 and SRES3 (A21, A22 and A23). These three scenarios are provided by the CICS webserver with latitude/longitude co-ordinates for all months of the year, therefore the files were extracted and converted to a comma-separated values file for import into ArcGIS. Grids were created and re-gridded in a 20 x 20 format for interpolation of evaporation levels for each lake site by month.

Hydrologic Atlas

The Canadian Hydrologic Atlas was created by denHartog and Ferguson (1978) to illustrate the spatial variation of hydrological parameters across Canada. The Atlas does not exist in digital format; therefore the mean annual lake evaporation (Plate 17) was scanned, geo-registered, and digitized in ArcGIS. Polygons were created for a buffered zone around the province of Alberta. The polygon data was used to create a 20 x 20 grid, and individual estimates of evaporation were extracted for each lake site by month.

Morton Fort McMurray Lake Estimate

The Morton model (Abraham 1999, Morton 1983) monthly averages estimates of lake evaporation for the area of Fort McMurray. The sum of the monthly values was included in the analysis for reference.

Precipitation and Temperature

ANUSPLIN

The 500 arc second ANUSPLIN data set (Hutchinson 2000, Price *et al.* 2000, McKenney at Canadian Forestry Service provided this data set for Canadian stations) was downloaded from the CICS website. The data set contains gridded monthly mean values for daily maximum and minimum air temperature and total precipitation for the 1961-1990 period. Average daily maximum and minimum monthly temperatures were averaged to get one value for each month of the climatology. The data was input into ArcGIS and generated into a coverage using the latitude and longitude co-ordinates provided. Grids were created and re-gridded to the 20x20 cell format, then each lake site was interpolated for all months of the year for both temperature and precipitation data.

CANGRID

The National Water Research Institute in Saskatoon provided the CANGRID data set for use in this analysis (Louie *et al.* 2002). A similar data set can be found on the Canadian Institute for Climate Studies (CICS) website[4]. This data set uses interpolated monthly temperature and precipitation climate data sets from 1895 to 1995 collected at nearly 350 Canadian monitoring stations, which has been adjusted for any bias or introduced error as a result of shifts in either station location or observational routines. The data set is built on a 50 km grid on a polar stereographic projection aligned along 110 degrees West. The data set was provided for all years and months from 1960 – 1990, therefore the climatology was created by averaging these years by each month for each station in the data set. The final climatologies were then covered to grids, and re-gridded to a 20m-grid cell. These were used to interpolated for each lake site by monthly iterations. CANGRID is known to perform well in mountainous terrain because it is includes additional checks and balances on this difficult-to-predict variable (Widmann and Bretherton 2000).

CRU 0.5-degree

The Climate Research Unit's half-degree mean monthly long-term climatology (New *et al.* 1999) was downloaded from the IPCC's website and formatted from NetCDF to a GIS grid using the procedure as outlined in the first section of this Appendix. The data had to be shifted from the co-ordinate system provided by the CRU/IPCC to a regular, Cartesian co-ordinate system.

CRU 10-minute

The Climate Research Unit's 10-minute climatology (New *et al.* 2002) is available for precipitation and temperature (New et al., 2002) in a 10-minute grid format, and is supplied with latitude and longitude data positions in the ascii array, which assisted the conversion of this data set to a GIS format. Once the data set was in the GIS, a grid was generated and then regridded to the standard 20x20 grid-cell format.

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[4] Web site address:
www.cics.uvic.ca/climate/CanadaGriddedClimateData/CanadaGriddedClimateDataDocumentation.htm

Inverse Distance Weighting (IDW)

Ron Hopkinson at the Meterological Service of Canada created the informally entitled inverse-distance weighted (IDW, McKenney *et al.* 2001.) data set. This data is interpolated station data from the 1960 – 1990 period to a 50km grid. The data set was downloaded from the CICS website where more detailed information can be found[5]. The data was downloaded from the CICS website and is supplied with latitude and longitude co-ordinates in the ascii array. The data was converted to a GIS grid format and then re-gridded to the 20x20m normal array.

Parameter-elevation Regressions on Independent Slopes Model (PRISM)

Chris Daly of Oregon State University developed the Parameter-elevation Regressions on Independent Slopes Model (PRISM) data set[6] (Daly *et al.* 1994). Long-term monthly means (1960 – 1990) for precipitation and temperature are available for BC, the Yukon and the Prairie provinces. The spatial resolution of PRISM is around 4 km which is critical in areas of high relief such as BC and the Yukon. This data set was provided by the National Water Research Institute and was provided with latitude and longitude format within its data array. The information was imported into the GIS, converted to shape file, clipped, and gridded to a 20m cell-size. This grid was used to interpolate lake site data.

NCEP/NCAR Reanalysis (Temperature Only)

NCEP/NCAR Reanalysis (Kalnay *et al.* 1996) temperature (ºC) data is published through the CDC and available in NetCDF format as a monthly long-term global mean surface level flux[7]. This data set is created using the averages of instantaneous values at four daily reference times: 0hr, 6hr, 12hr and 18 hours over the monthly period for 1960 – 1990 time frame. The data is provided in a spatial format of 2.5-degree latitude x 2.5-degree longitude global grid with 144x73 points. Data were converted using the process outlined in Section X, inclusive of the X, Y shift. Grids were created in ArcGIS and then re-gridded to match the 20x20m standard grid format. Lake site data was extracted from this normal grid.

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[5] Web site address: www.cics.uvic.ca/climate/data.htm

[6] See: www.ocs.orst.edu/prism/prism_new.html).

[7] Web site address: www.cdc.noaa.gov/cdc/data.ncep.reanalysis.derived.html

Relative Humidity

CRU 10-minute

The Climate Research Unit's 10-minute climatology is available for relative humidity (New *et al.* 2002) in a 10-minute grid format. It is supplied with latitude and longitude data positions within the ascii array, which assists the conversion of this data set to a GIS format. Once the data set was in the GIS, a grid was generated and then re-gridded to the standard 20x20 grid-cell format.

Hadley

The CICS website provides access to the Hadley HADCM3 (Pope *et al.* 2000) model data set for relative humidity. Researchers at the Hadley Centre created the Hadley GCM for global climate modelling. For this reason, the data is coarse (2.5 x 3.75°) and not as effective at capturing spatial variation in humidity values across the study sites.

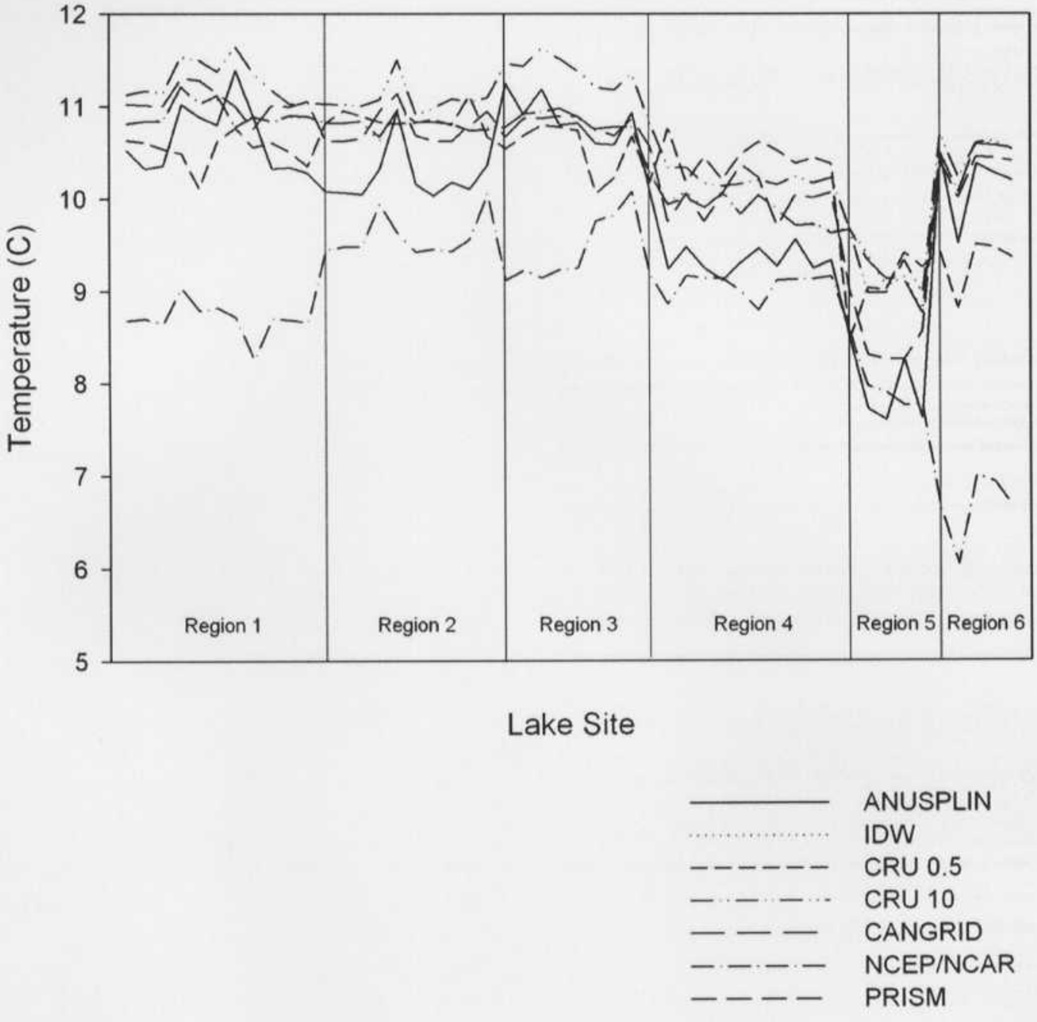
NCEP/NCAR Reanalysis Surface and 1000mb

NCEP/NCAR Reanalysis (Kalnay *et al.* 1996) Relative humidity (%) data is published through the CDC and available in NetCDF format as a monthly long-term global mean surface level and 1000mb flux[2]. This data set is created using the averages of instantaneous values at four daily reference times 0hr, 6hr, 12hr and 18 hours over the monthly period for 1960 – 1990 time frame. The data is provided in a spatial format of 2.5° x 2.5° global grid with 144x73 points. Data were converted using the process outlined in Section X, inclusive of the X, Y shift. Grids were created in ArcGIS and then re-gridded to match the 20 x 20m standard grid format. Lake site data was extracted from this normal grid.

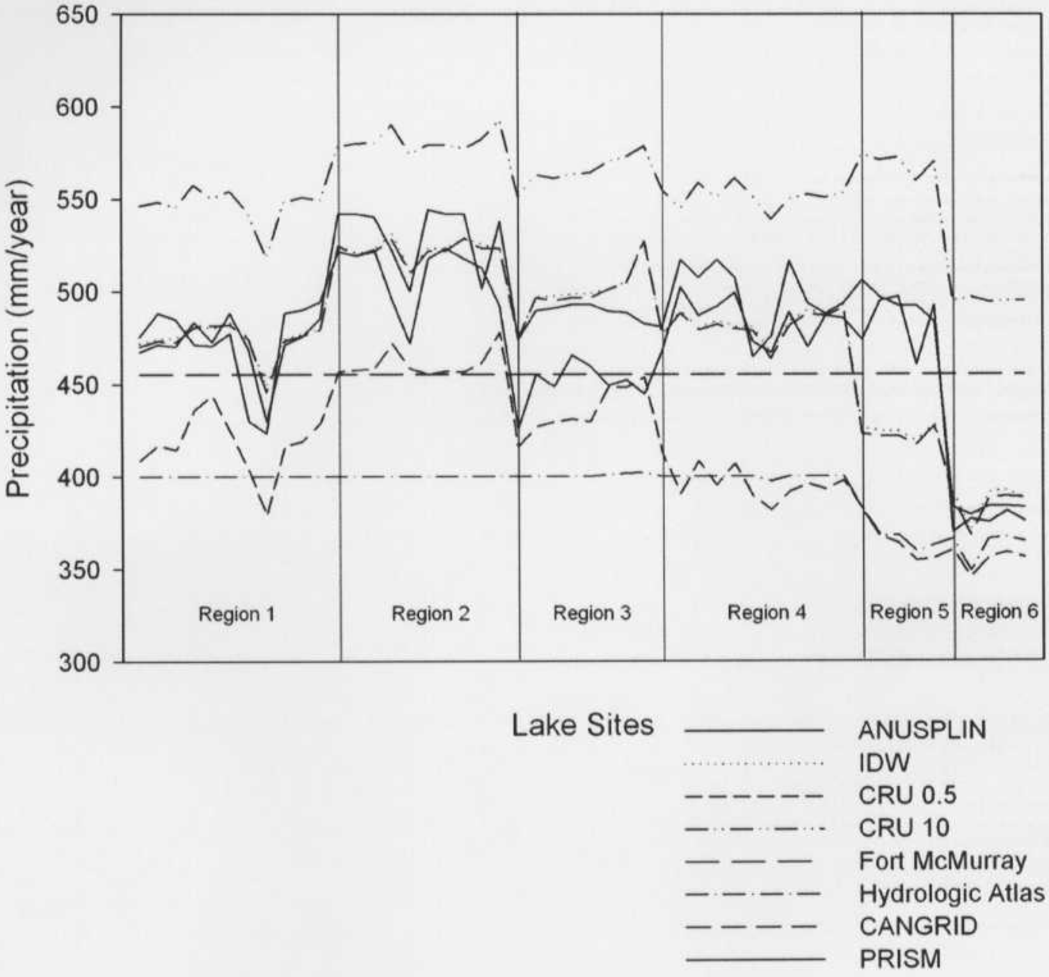
ECMWF

The ECMWF 40-year reanalysis (Uppala 2001) monthly daily mean (averaged over six-hourly observations) relative humidity data was downloaded for the period of 1960 – 1990 in NetCDF format for North America in a 2.5° x 2.5° (29 x 17) array. The NetCDF file format was unpacked for each monthly file and converted to a text file, re-formated with appropriate header information. The files were then input into ArcGIS as grids, which were re-gridded to the 20m x 20m format to allow for interpolation at each lake site by month.

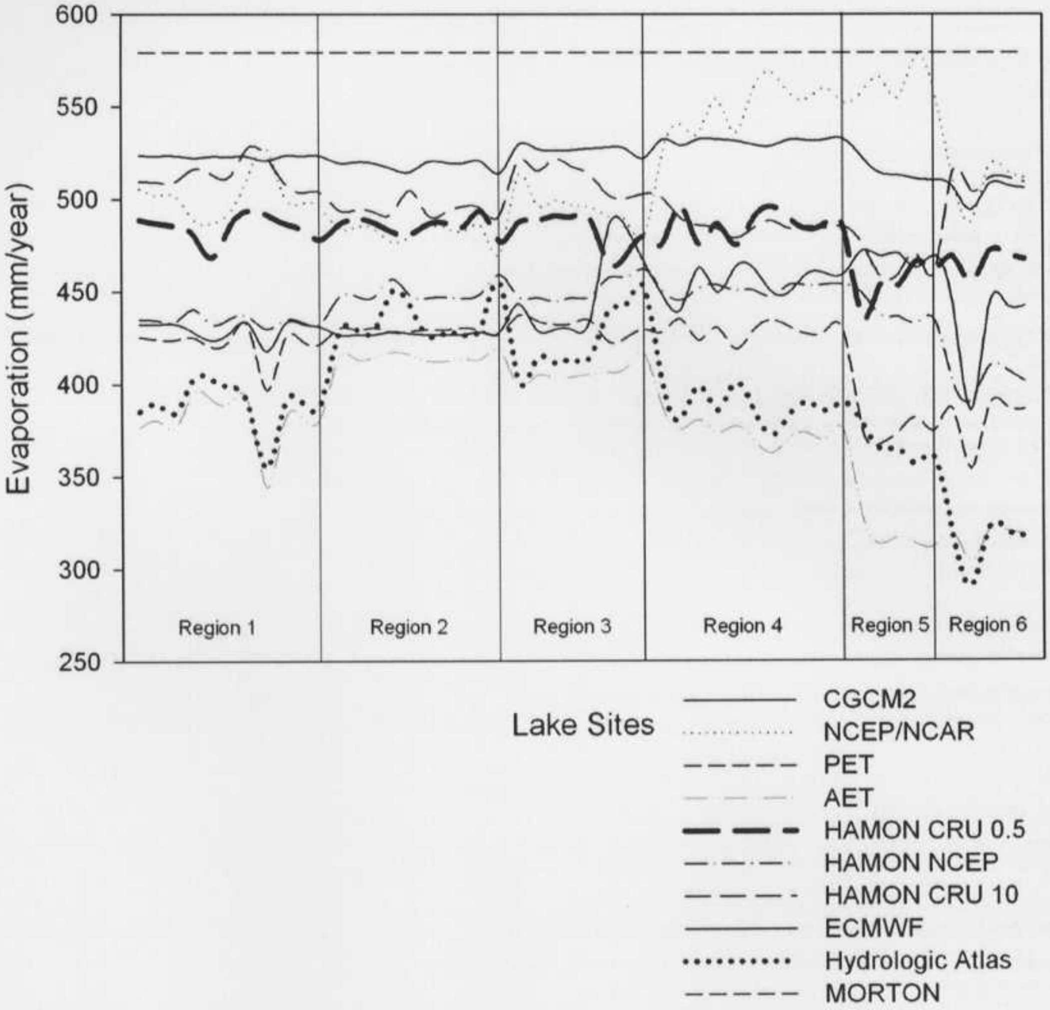
Temperature Results



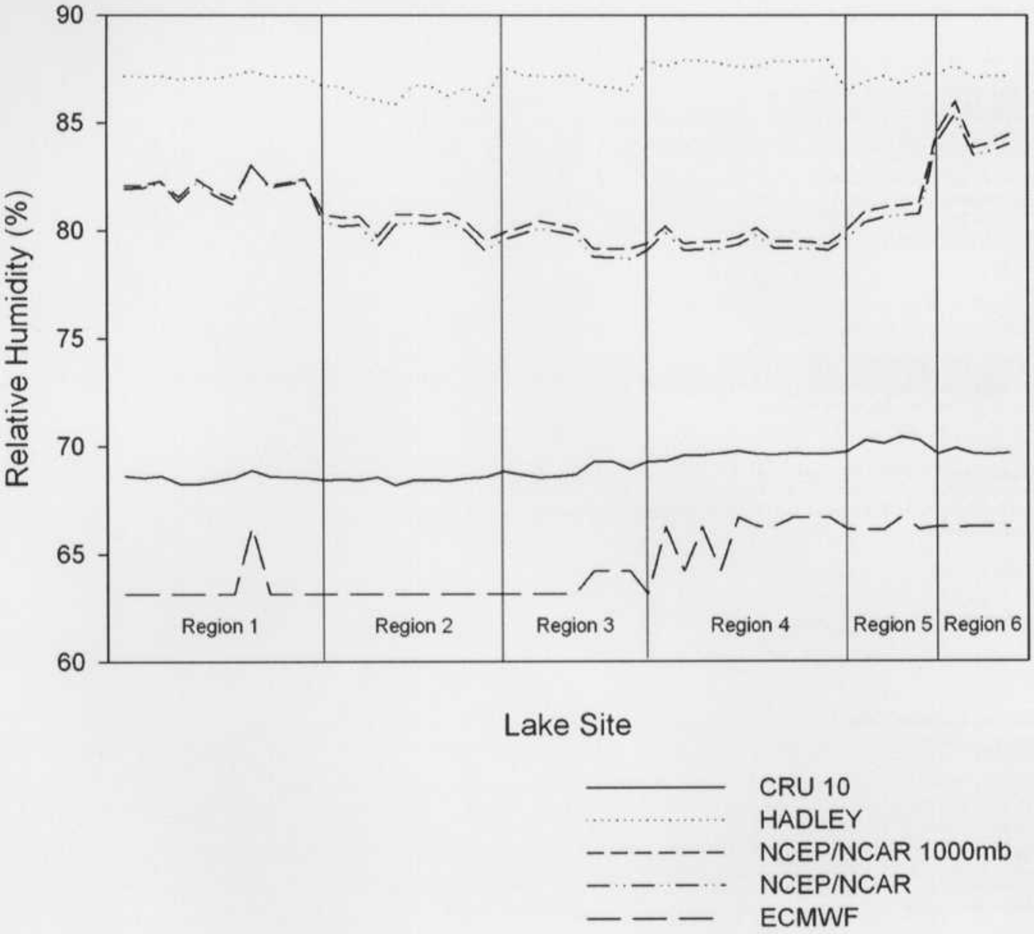
Precipitation Results



Evaporation Results



Relative Humidity Results



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Appendix B: DETAILED LAKE STUDIES

Results from the detailed lake studies undertaken as a component of the seasonal monitoring program carried out in summer 2004 illustrate that each of the lakes under study have different hydrologic interactions occurring between their input isotopic water signals (δ_P), seasonal lake water isotopic fluxes, open water contributions (wetlands and lakes) and groundwater interactions. General conclusions can be made based on specific occurrences of events, such as systematic isotopic enrichment of precipitation samples, and or groundwater positions found at all study sites. Some unique properties of lake systems are also apparent from the results and insight gained from this exercise. Results are illustrated in figure at the end of this appendix.

Five systems were monitored for shallow groundwater, precipitation, lake water flux, inflows and outflows, when present (NE7, NE11, SM9, BM7, and SM7), while one lake system (BM10) had several open water systems within its watershed, which were monitored over the summer season. Lake samples collected are shown in Figures with closed, coloured squares, while annual averages for the period 2002 – 2004 are given with open circles. Open, large squares illustrate outflow signals, and inflows are shown with small closed triangles. Closed diamonds represent monthly precipitation collected at study sites, the summer (June to September) average station data (CNIP) from Edmonton (-14.27, -109.25‰) is shown with a star and modelled precipitation for the lake sites is shown with an open diamond.

The shallow groundwater samples are represented by open triangles, found generally within a range of –15 to –20‰ for $\delta^{18}O$ and –130 to –160‰ for δ^2H. The CNIP line is shown on each graph and the plots of water samples denote the relationship between $\delta^{18}O$ and δ^2H for each hydrologic node. BM10 is shown in a slightly different context, as no detailed groundwater sampling was performed at this lake, rather a number of different open water sources provided an opportunity to examine the isotopic shifts through the season at each point and along the continuum from wetlands to an inflow lake system to the study lake. For all water samples, representative shapes are shown with colour coding for June through September, dark blue shapes illustrate samples collected in June, pink is July collection, August sampling is shown in red and September is shown in green.

Lake water and precipitation isotopic signatures vary depending on the season and the site. Generally, lake water signals progress through from a low isotopic enrichment in June, based on snowmelt inputs residing in the system through to an enrichment peak in August, which then regresses back towards a less enriched state, sometimes falling near to the July isotopic position. Isotopic signatures for precipitation collected at gauges installed in the catchments are highest in July at nine of the seasonal study catchments with the exception of SM7, where August precipitation values are higher. Lake SM7 also experienced greater precipitation input during August, while the remainder of the gauges recorded July precipitation as significantly lower than either August or September collection periods. SM7 is also the most southern site in the 50-lake network. The very high values recorded in July, therefore could also be an artefact of systematic error occurring due to the gauge design. Low amount of rainfall could have resulted from compounded errors due to trace amounts of evaporation occurring within the gauge collection funnel, or perhaps the mineral oil cap was not effective at containing evaporation (see methods in Chapter 1 of this thesis). However, upon inspection of the CNIP data set for Edmonton during the twelve months of the year, July is the most enriched signal present in the dataset, and given that these high values occur in July at nine of the sites analysed, potential sampling error or analytical error is overruled. Another issue with isotopic signals in precipitation is that the samples collected and analysed from lake sites are higher than the modelled isotopic signal in precipitation, as the values observed in catchments have not been amount weighted. Modelled precipitation isotopic signatures fall within the range of measured shallow groundwater isotopic signatures in every case, except at BM7, where the modelled precipitation input is slightly more enriched than the groundwater signals.

Shallow groundwater signals collected from mini piezometers in five catchments show that groundwater does not flux to the degree observed in precipitation or lake water isotopic samples. In general, groundwater is most depleted in June, and is most enriched in September. Groundwater signals appear to be contributing to lake water, reversals observed in more southern studies (Devito and Ferone, 2004) are not occurring at four of the five lakes studied. Even in the cases where groundwater piezometers were located nearby (< 10m) the lakeshore, groundwater signals are still more depleted than the lake water isotopic signatures. In the case of lake NE7, for example, the closest piezometer to the lake edge did not have a similar isotopic signature, rather the piezometer furthest away from the lake system had the highest amount of enrichment, indicating the complexity of groundwater flow pathways occurring within these systems which may be based in part on substrate and vegetation characteristics.

Throughflow lake systems such as lake NE7 and BM7 have signatures similar to groundwater, which indicate that these systems may be closely connected to their groundwater sources and are being maintained completely by groundwater hydrologic connections, which allows for sustainability of water resources over the summer periods, lending to shortened residence times and lower evaporation rates in the lake system. Lakes such as NE11 and SM9, and at the extreme evaporative end, SM7 are not in close connection with their groundwater sources. Groundwater reversals could be expected at these sites, indeed the only evidence is found at lake SM7, where the lakeshore piezometers were depleted during June, but as the summer progressed these groundwater wells exhibit isotopic signals trending towards the lake signals, closer to –15‰ $\delta^{18}O$ and –130‰ $\delta^{2}H$, on the enriched margin of all groundwater signals observed in the study. SM7 was observed to have high amounts of bog in its catchment, therefore may experience reversals as vegetation begins to draw from the lake since it is not able to obtain adequate water from the bog systems, and/or if the bog systems begin to require the water as their water tables begin to draw down after the heavier rains observed earlier in the season begin to wane. However, the potential groundwater reversals occurring at lake SM7 require further investigation to determine if this is the case.

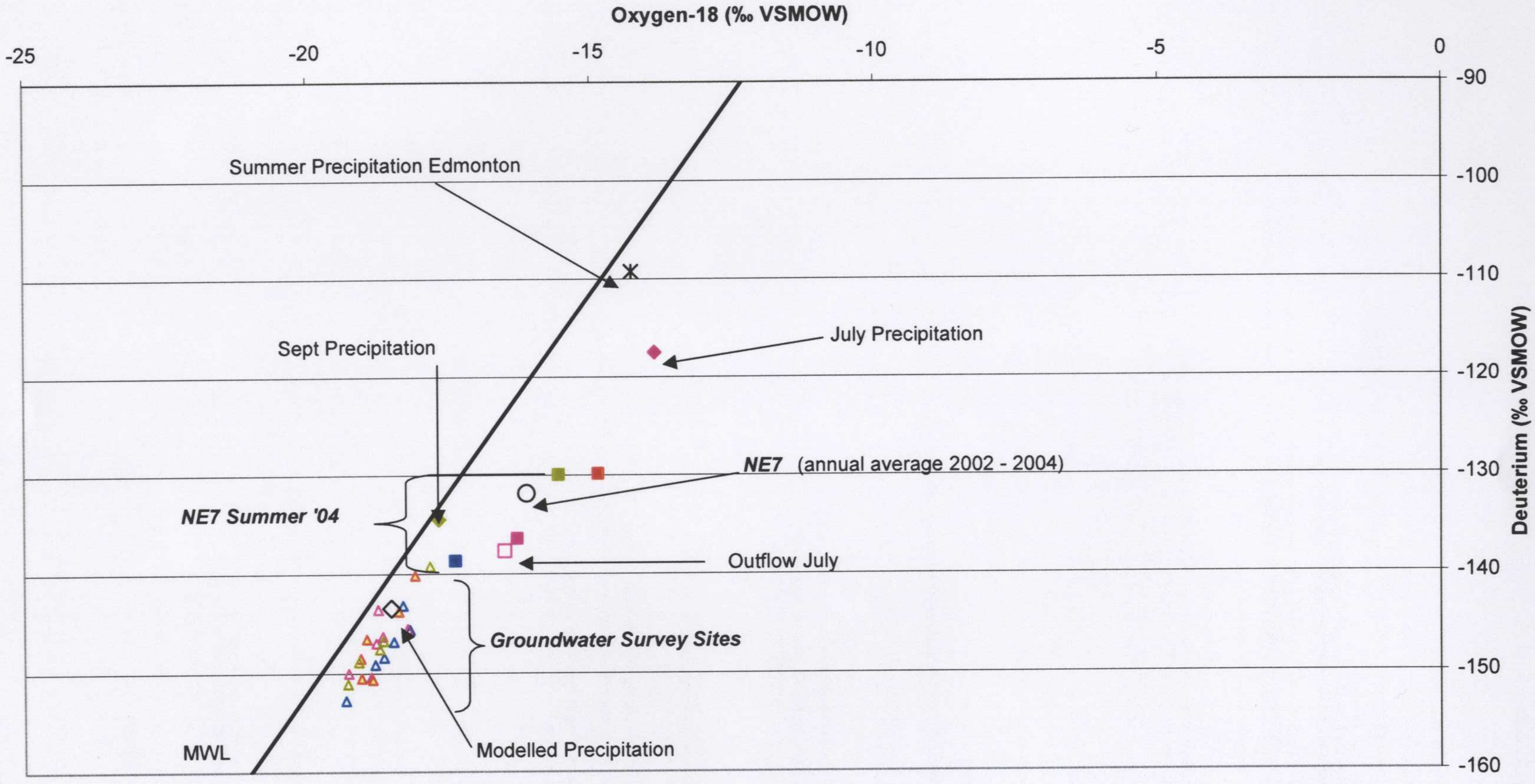
NE11, SM9, BM7 and SM7 catchments each contain inflow systems located within their watersheds, including small open water bodies, wetlands and rivers that may be feeding them evaporated water and/or their groundwater inputs to the lake may be constrained by wetland features found within their catchments. NE11 watershed contains two rivers that merge into a single system, and inflow into the lake, namely Iyinimim Creek and South Creek. The inflow, where its channel meets the lakeshore was sampled in June just above its mouth and Iyinimin Creek was sampled in August. The isotopic signatures from the inflow systems indicate that most of the runoff is coming from Iyininim Creek and/or that South Creek is very similar isotopically to Iyinimin.

Additionally, these rivers have isotopic signatures that do not flux greatly over the sampling period, indicating that they have a consistent source of water feeding them throughout the ice-free season. Being isotopically close to the groundwater signals taken from NE11 shallow groundwater stations, a hypothesis is posed that these systems are fed by groundwater runoff from the hills located in the uplands of the NE11 watershed. SM9's inflow is isotopically stable over the three-month period it was monitored, which indicates perhaps that it is sustained by groundwater systems. This is important to note, because if examined topographically, this small lake has only a narrow band of treed catchment surrounding it, and therefore its sustainability during the open water season would otherwise pose a hydrologic mystery.

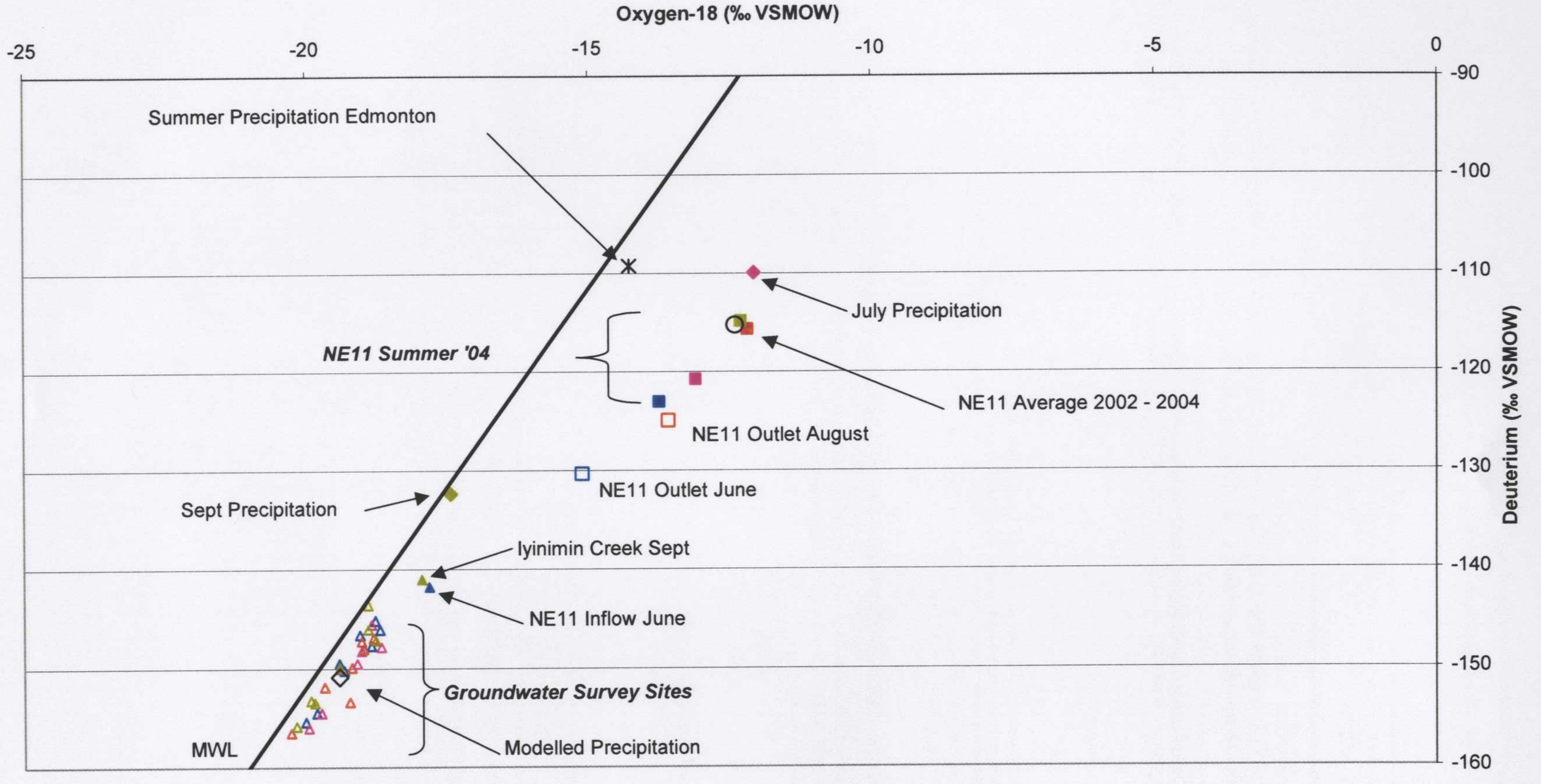
The groundwater catchment boundary must be larger than the topographic bounds (Devito *et al.*, 2005), or the groundwater system feeding this lake could be very slow to deliver water but still remain a consistent source, such as a fen wetland. Inflows to BM7 are also an interesting case, in June the inflow fen is completely fed by groundwater sources, but through July and into September the inflow becomes more evaporative and/or dominated by input precipitation sources. BM7 is also the only lake system where September precipitation signals fall into the range of groundwater signals. The highest amount of precipitation was observed in rain gauges at this site during the September period. An inflow lake to SM7 was found to be more evaporative than the lake system, indicating that while it is a contributing source, it may not be connected to groundwater inputs, or perhaps this result is indicative of catchment characteristics at SM7. It is theorized that lake SM7 and its associated watershed may be heavily influenced by the bog systems found in the area, which tend to hold their water rather than channel and release it as fens are known to do.

Outlets were also sampled at two lake systems, providing an indication of the relationship between the lake outlets and the lake system. Two samples from the NE11 outlet were taken during June and August; results indicate that these systems are more throughflow than the lake system. NE7, which is a throughflow lake system, has an outlet signature similar to the lake system, which is not surprising given that the lake is likely pumping through its water to its outlet in a rapid manner during the summer months. However, given that NE11 recharges at a moderate rate, the throughflow nature of the outlet signal suggests that the outlet may be fed by groundwater systems not in connection with the lake. This is surprising given the very slow nature of the outlet observed during the August sampling periods, where the water in the river channel was essentially stagnant.

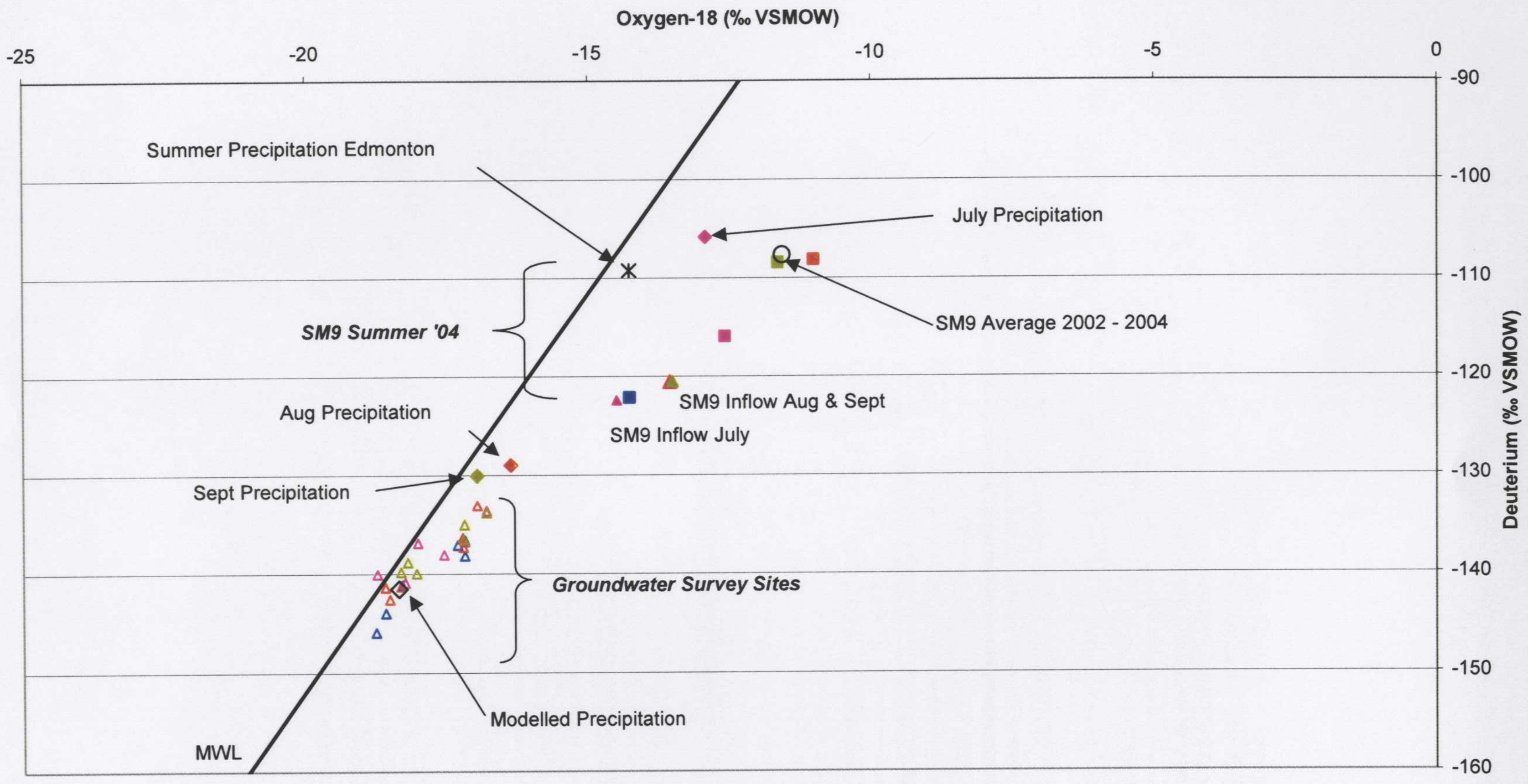
BM10 contains three feeder systems in its watershed, two wetlands and a large lake which inflow into the study system. BM10 and its inflow lake are very close isotopically, at all months of the survey. The upper lake and in particular the wetland system have larger ranges of isotopic signal through the summer periods. Although the wetland was not sampled in August, from all other samples we can infer that August would have been close isotopically to signals observed during that month at BM10. These results confer with research on small lakes and wetlands and the variability exhibited in isotopic ranges, owing to high evaporation rates at these confined, small shallow systems. The wetlands and the inflow lake systems all contribute to the isotopic signal and the evaporative state present in BM10, a nice example of the continuum of evaporative enrichment that can occur through a system, and the importance of measuring headwater lakes during studies to minimize the error within water balance modelling associated with the challenges of estimating more evaporative bodies.



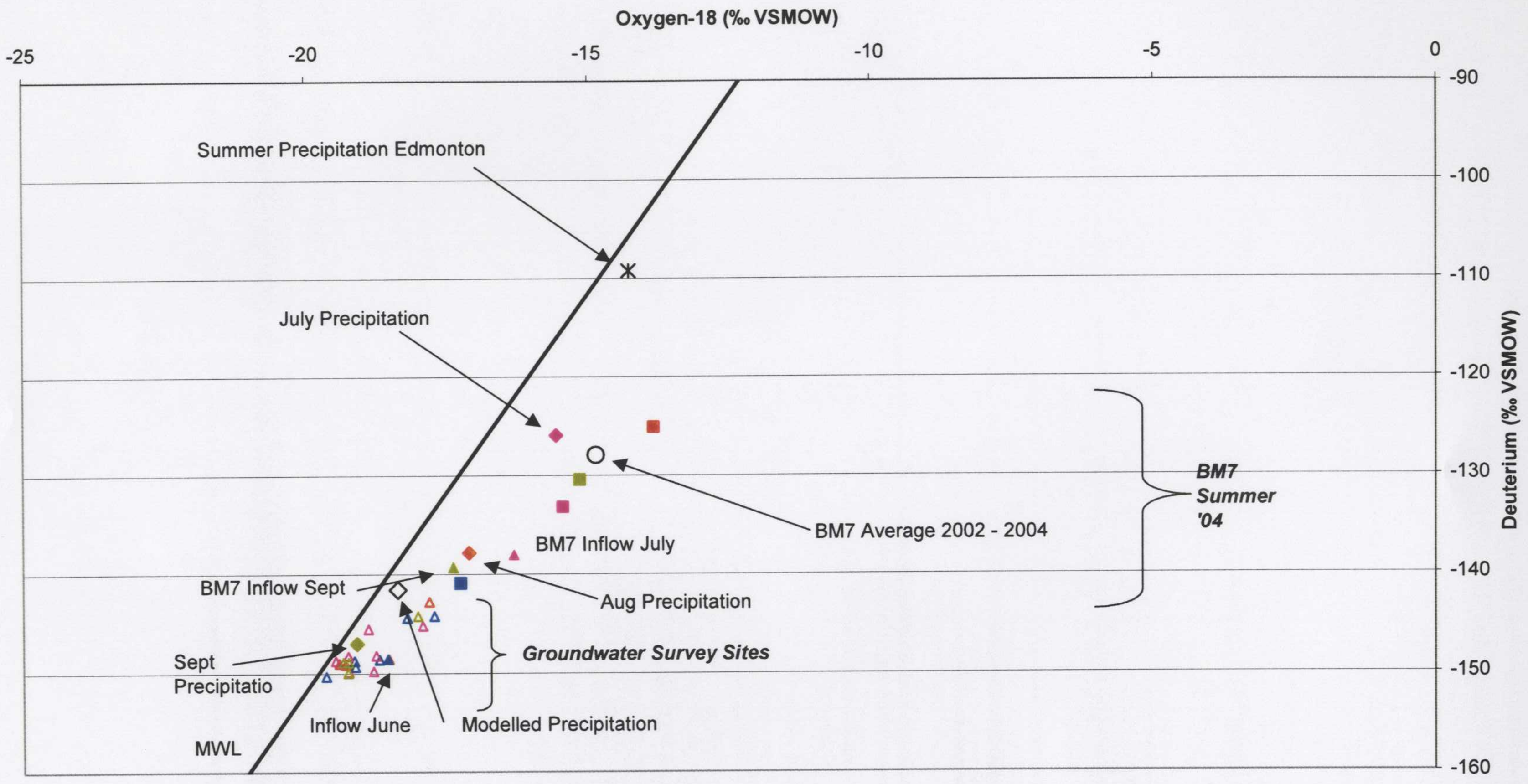
Detailed Study at NE7.



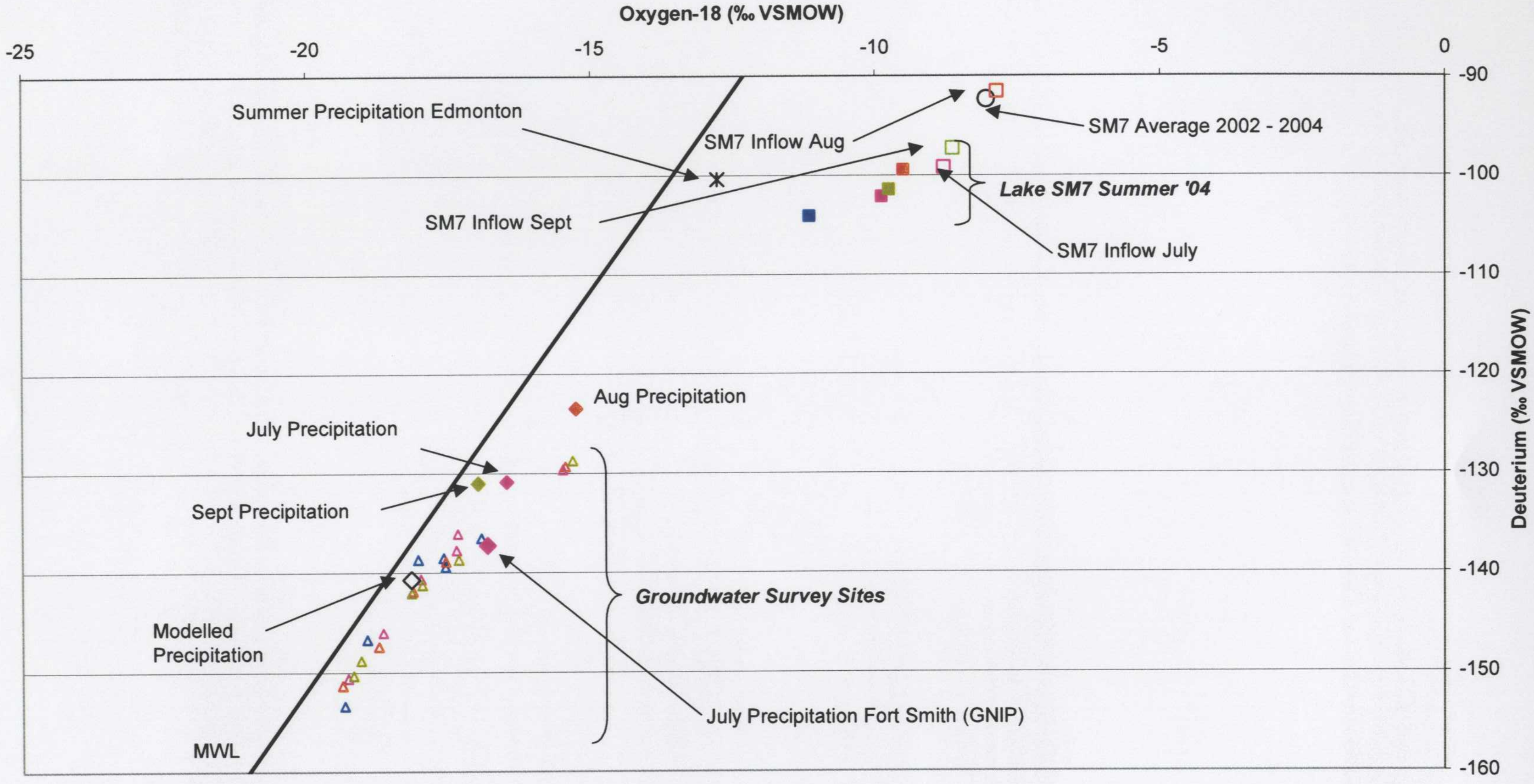
Detailed Study at NE11.



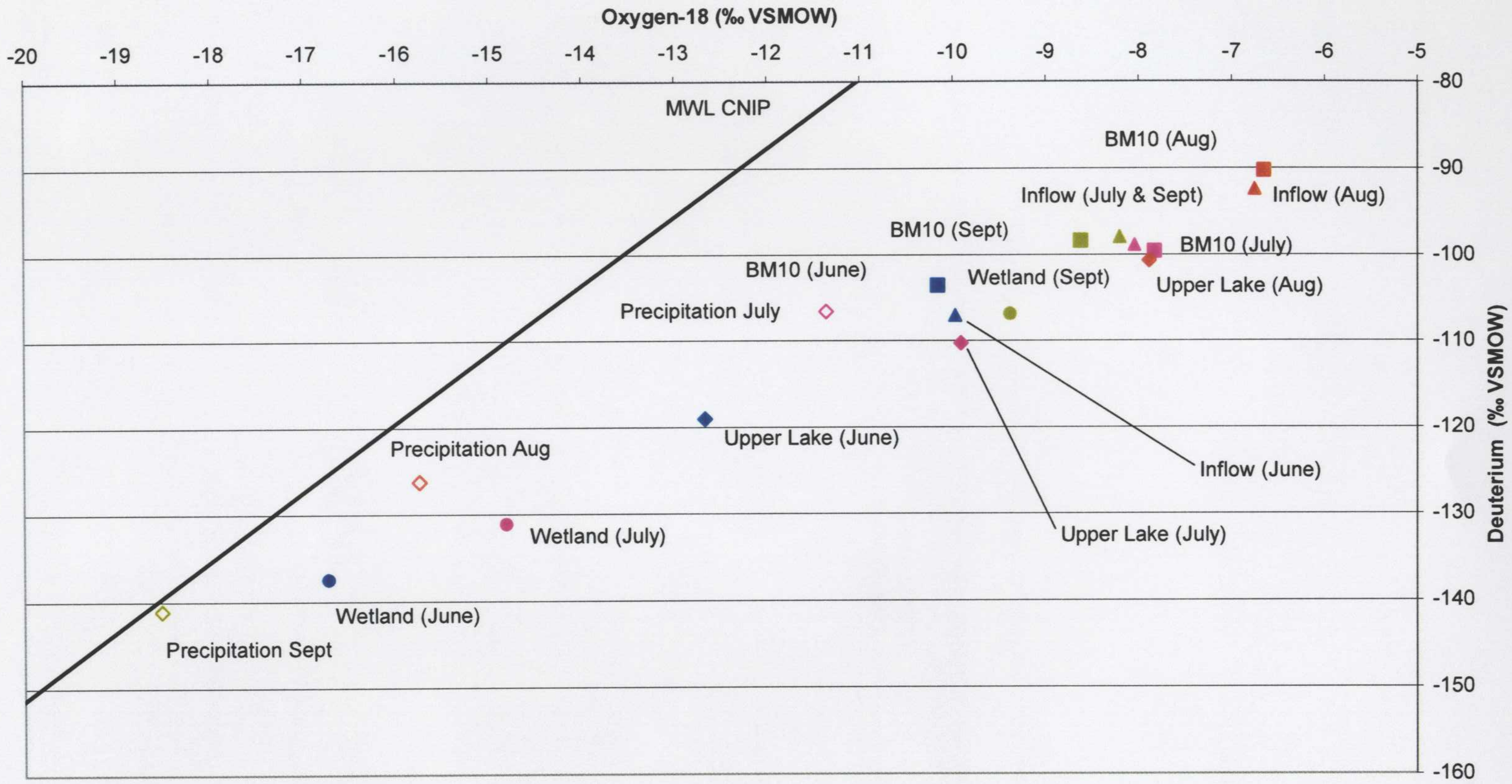
Detailed Study at SM9.



Detailed Study at BM7.



Detailed Study at SM7.



Detailed Study at BM10 - Hydrologic Nodes.

Appendix C: TRANSFORMATIONS

Variable or Parameter	*Transformation*
Latitude (LAT)	Ln (LAT)
Lake surface area (LSA)	Ln (LSA + 0.005)
Lake perimeter (LKPER)	Ln (LKPER + 0.005)
Drainage basin area (DBA)	Ln (DBA)
Max depth (MAXDEPTH)	1/(SQRT MAXDEPTH)
Average depth (AVGDEPTH)	1/(SQRT AVGDEPTH)
Lake elevation (ELEV)	Ln (ELEV + 1)
Catchment elevation (CELEV)	Ln (CELEV + 1)
Volume (VOL)	SQRT (1/VOL)
Slope maximum (MAXSLOPE)	Ln (MAXSLOPE + 0.001)
Slope average (AVGSLOPE)	Ln (AVGSLOPE + 0.005)
E/I ratio (EI)	Ln (EI + 0.05)
Water yield (WY)	Ln (WY + 0.025)
Residence time (RT)	Ln (RT)
Drainage ratio (DR)	Ln (DR + 1)
Drainage ratio^{-1} (DR^{-1})	Ln (DR^{-1})
Perimeter/lake volume (PVOL)	Ln (PVOL)
Net catchment area/lake volume (NCALVOL)	Ln (NCALVOL + 1)
Runoff/precipitation (RP)	Ln (RP)
Effective drainage basin area (eDBA)	Ln (eDBA + 0.25)
Wetland (%) (WET%)	Arcsin (WET%)
Upland (%) (UP%)	Arcsin (UP%)
Bog (%, AVI) (BOGA)	Arcsin (BOGA)
Fen (%, AVI) (FENA)	Arcsin (FENA)
Conifer (%, AVI) (CONF)	Arcsin (CONF)
Deciduous (%, AVI) (DECID)	Arcsin (DECID)
$NH4^+$	Ln ($NH4^+$ + 0.0025)
$NO_2 NO_3$	Ln ($NO_2 NO_3$ + 0.025)
TDN	Ln (TDN)
TKN	Ln (TKN)
TN	Ln (TN)
TP	Ln (1/TP + 0.01)
TDP	Ln (1/TDP + 0.05)
DOC	Ln (DOC)
DIC	Ln (1/DIC + 0.05)
Cl	Ln (Cl)
SO_4	Ln (SO_4 + 0.005)
Na	Ln (Na +0.025)
K	Ln (K +1)
Ca	Ln (Ca)
Mg	Ln (Mg)
Fe	Ln (Fe)
Si	Ln (Si + 0.22)
ALK	Ln (ALK)
BIC	Ln (BIC)
COND	Ln (COND)
pH	Ln (pH + 0.025)
Colour	Ln (COL + 1)
Secchi	Ln (SECCHI + 0.005)

Ln = log normal (base 2)