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Predicting mixing trends in mine-receiving waters using water quality modeling

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Predicting Mixing Trends in Mine-Receiving Waters Using Water Quality Modeling

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This thesis has been prepared

under my supervision

and the candidate has complied

with the Master's regulations.

Signature of Supervisor

Date

Abstract

Complete mixing of the water column of lakes is important to ensure that nutrients and dissolved oxygen are replenished and equalized throughout the lake. This ensures that organisms within the lake at all trophic levels can perform necessarily metabolism and have a maximized habitat range. Lakes that receive effluent high in total dissolved solids from mine operations can be prevented from performing complete water column turnover. When this occurs the lake is termed meromictic. Two lakes, one naturally remediating and the other actively receiving effluent discharge, have both exhibited historical meromictic conditions (meromixis). Over a three year period, the water quality in both lakes was analyzed and related to their current meromictic state. The CE-QUAL-W2 model was calibrated to predict total dissolved solids concentrations within the active receiver lake and one-year predictive simulations were run with total dissolved solids reductions of 10%, 25%, 50% and 75% at the lake inflow. The lake undergoing natural remediation exhibited substantial breakdown of meromictic stability during the study and was deemed monomictic while the active receiver demonstrated meromictic stability and variability in mixolimnion turnover depth. Calibration of CE-QUAL-W2 revealed that fluctuations in surface total dissolved solid concentrations and dissolved organic carbon from natural and effluent inputs had substantial influences on heat distribution in the effluent receiver. Reducing total dissolved solids inputs into the active receiver lake only elicited change in mixolimnion total dissolved solids concentrations but little change in monimolimnion concentrations. The 50% and 75% reduction simulations resulted in a much shallower mixolimnion depth and stronger meromictic stability in the lake.

Lay Summary

The Lakehead University Department of Biology mission statement is as follows, "Faculty and students in the Department of Biology are bound together by a common interest in explaining the diversity of life, the fit between form and function, and the distribution and abundance of organisms." This project is focused on the limnological science field of biology. Within an aquatic habitat, water column mixing controls feeding and reproduction habits of organisms across many trophic levels. Water column mixing controls the distribution of heat and availability of nutrients and oxygen for these organisms. Researching and modeling how lakes physically and chemically respond and progress through mixing alterations due to industrial influence is an essential first step to understanding how the biotic components of the lake also respond. The goals and discoveries of this thesis will not only outline the future health and state of the study lakes but will also attempt to relate this to improvement in habitat as well.

Acknowledgements

The great and many challenges I faced during the evolution of this project could not have been overcome without the support and motivation from my parents, grandparents, sisters and girlfriend.

I would like to thank Dr. Peter Lee for originally asking me to be a part of the project and for having a great deal of patience and guidance during the project's duration. I would also like to thank my committee (Dr. Wensheng Qin, Dr. Stephen Hecnar and Dr. Amanda Diochon) for their patience, academic guidance and critique.

A great deal of thanks is owed to Barrick's Hemlo Gold Mine Environmental Department including Shane Hayes, Jeremy Dart, Myles Michano, Greg Petten and Tess Petkevicius for their support, flexibility and time out in the rain, snow and heat during field data collection. You are worth your weight in gold! I hope you also learned something along the way.

Dr. Robert Annear Jr. also deserves a shout out for his donated time to chat with me about CE-QUAL-W2 model set-up and theory.

Finally, I would like to dedicate the project to my two grandfathers, Dieter and John-Joe, who passed away while writing the project but will continually motivate me to be better every day.

"If you can't do great things, do small things great."

"I haven't failed, I've just found 1000 ways that don't work."

"Obstacles are what's seen when you've lost sight of the goal."

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General Introduction

Water Quality of Gold Mining Effluent Discharge

Water is used as the medium for the chemical reactions that extract gold from the ore (gold-containing rock) in the milling processes at gold mines. Many reagents are added to the process water to optimize gold extraction. Although the reagents used can vary depending on the extraction process, common reagents include calcium hydroxide ($Ca(OH)_2$), sodium hydroxide ($NaOH$), sodium cyanide ($NaCN$), potassium amyl xanthate (PAX) and copper sulphate ($CuSO_4$). These reagents aid in efficient removal of gold from the ore and balancing of pH within the mill process. After gold removal, the mill process water is treated. Cyanide is removed via sulphur dioxide treatment (Devuyst EA *et al* 1989) and metal removal utilizes either ferric chloride ($FeCl$) or ferric sulphate ($Fe_3(SO_4)_2$) to precipitate and collect the heavy metals as a floc/colloid (Matilainen *et al* 2005, Veolia 2011) and $Ca(OH)_2$ to balance pH. Even after treatment, the discharge water (effluent) typically still contains elevated concentrations of calcium (Ca^{2+}), chloride (Cl^-), sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+) and sulphate (SO_4^{-2}) that can be sourced to either the mill reagents or the chemical composition of the ore itself. These elevated ion concentrations quickly increase the salinity and density of the freshwater systems receiving the effluent and can alter natural water column mixing and flow patterns. Many biological and chemical cycles are altered as a result of elevating ion concentrations in freshwater lakes, however, the focus here will largely be on the effects of water column mixing.

Lake Mixing: Dimictic Lakes

Lakes in which the whole water column mixes or turns-over are classified as holomictic and when this turnover occurs twice annually, the lake is further classified as dimictic (Hutchinson and Loffler 1955, Lewis 1983). Depending on latitude, this commonly occurs during spring and fall. These lakes are termed dimictic because they mix twice per year. Water column mixing, although controlled by many variables, is influenced in large part by the strength of the density gradient across the water column, from the lake surface, to the lake sediment (Birge 1916, Hutchinson 1957, Schmidt 1928, Walker 1974, Hakala 2004). A water-column density gradient can be attributed to a difference in temperature and/or salinity. When discussing this gradient in relation to either temperature or salinity, the terms thermal stability and chemical stability are used, respectively. The larger the difference in temperature and/or salinity across the water, the stronger the density gradient and the more work or energy needed for complete water column mixing (Birge 1916, Schmidt 1928). Since a majority of Canada's freshwater lakes have relatively low background salinity (Armstrong FAJ and Schindler DW 1971, Moser *et al* 1998), most density gradients within these lakes result from changes in water temperature influenced by hot summers and cold, ice-forming winters. Therefore, temperature has dominant control over water column mixing in a majority of Canada's freshwater lakes. This is why these lakes are able to mix in the spring and fall; when the temperature gradient deteriorates and the lake becomes isothermal (same temp from surface to bottom) (Hutchinson and Loffler 1955).

Temperature gradients generally produce three distinct layers (strata) within a water body: the epilimnion, metalimnion and hypolimnion (Hutchinson 1957, Imberger 1985). The epilimnion contains low-density, warm water in the surface strata while the hypolimnion contains high-density, cold water in the lower strata (Hutchinson 1957, Imberger 1985). The epi- and hypolimnions are separated by a stratum of rapid temperature change known as the metalimnion and on a plot of depth vs. temperature; the linear gradient of temperature change within the metalimnion is the thermocline (Hutchinson 1957, Imberger 1985).

Lake Mixing: Meromictic Lakes

The dimictic, seasonal cycle of water column mixing (turnover) can be altered if a large input of saline water into a freshwater lake occurs, such as releases of effluent from mining operations. This influx of highly saline water can cause salinity to have the dominant control of water column density rather than temperature (Walker 1974, Miller *et al* 1993). If a strong salinity gradient develops, there will still be resistance for the lake to fully mix, even if isothermal temperatures occur. A lake where full water column turnover is not possible is termed a meromictic lake (Findenegg 1935, Lewis 1983, Northcote and Halsey 1969) and the lake is said to have meromictic stability. If meromictic conditions result from saline water introduction from surface inflow, it is more specifically termed ectogenic meromixis (Boehrer and Schultze 2008, Ficker *et al* 2011, Hutchinson 1957). In a freshwater receiving environment, saline water will plunge towards the lake bottom because it is more dense than the water contained within the lake (Hogg *et al* 2013, Imberger and Hamblin 1982). If a large enough volume of saline water is introduced, a mixolimnion (low-salinity, surface-water strata) overlaying a monimolimnion (high-salinity, deep-water strata) will result (Findenegg 1935, Hutchinson 1937). The stratum of rapid salinity change between these layers is termed the chemolimnion and contains the linear chemocline gradient (Hutchinson 1937) (Figure I). Mixo- and monimolimnion strata will be unable to mix with each other because of the difference in density between them (Hutchinson 1957, Boehrer and Schultze 2008). True meromictic conditions are defined by the maintained presence and stability of these layers through turnover events. The low-salinity mixolimnion is maintained by settling of ionic compounds to lower strata and low-salinity precipitation and melt-water run-off (Boehrer and Schultze 2008). The mixolimnion has the ability to mix within itself during isothermal conditions in the spring and fall, and the mixolimnion depth and turnover depth are the same during this time (Boehrer and Schultze 2008). The mixolimnion also contains the thermal layers present in a typical thermally-stratified lake (epi-, meta- and hypolimnion) (Boehrer and Schultze 2008). The monimolimnion has the ability to mix within itself as well, although to a lower extent (Likens and Hasler 1960). This is similar to mixing that can occur within the hypolimnion of a thermally-stratified lake (Hutchinson 1938, McCarter *et al* 1952).

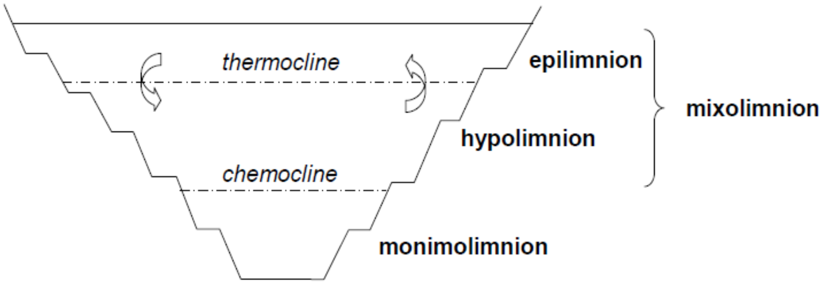


Figure I. Schematic of the layers within a meromictic lake (modified from Gammon *et al* 2009). Layers not proportionally represented.

Variables Affecting Lake Mixing and Meromictic Events

After meromixis has established in a lake, a variety of natural processes that can progress the lake back towards holomixis (complete turnover) by equalizing the density of mixo- and monimolimnion waters. Attempting to predict lake mixing events and if holomixis will reoccur requires understanding of the dominant mechanisms and lake characteristics that affect mixing within a specific study lake. Some of these mechanisms and characteristics may include wind effects, topographic sheltering, solar radiation/heating, bathymetry, basin morphometry, precipitation, evaporation and surface inflow/outflow location and water quality. Each lake system is physically and chemically unique and there is variability in which characteristics and mechanisms are dominant in regulating whether meromictic stratification is maintained or deteriorated. Each meromictic lake progresses uniquely through a meromictic event.

Wind Effects and Topographic Sheltering

Lake mixing and meromictic stability are largely affected by wind action on the lake surface (Birge 1916, Walker 1974). The magnitude of the wind's effect on a lake is site specific and varies depending on wind characteristics, such as speed and direction, sheltering structures such as topography and vegetation and lake characteristics such as fetch and bathymetry. These variables are dynamically linked and their effect on wind-induced lake mixing has been studied in the laboratory using wind tunnels (Markfort *et al* 2010) as well as in the field, utilizing meteorological stations situated at various lake locations while simultaneously measuring water temperature changes at depth (Huber *et al* 2008). The roughness and height of surrounding topography and vegetation dictates its wind-sheltering ability and the effect of these variables can change since lake shorelines often have heterogeneous composition (forest, wetland, grassland, mountains etc.). If wind direction changes, there is also change in the fetch and the sheltering structures the wind interacts with prior to reaching the lake. Long Lake in Washington is an example where the predominant wind direction and fetch directly impact water quality (Berger *et al* 2004). Due to lake orientation and pre-dominant wind direction, cyanobacteria populations are pushed to one end of this reservoir, impacting temperature as well as dissolved oxygen (DO) levels. Wind speed also contributes to the effect of the wind on lake mixing and water quality. It was found that high wind speeds experienced by an open pit lake for a period of four days forced a lowering of the thermocline by ~10 m (Huber *et al* 2008).

Lake Mary and Stewart's Dark Lake in Wisconsin, Hall Lake in Washington and Yellow Lake in British Columbia are lakes where meromictic stability persists even though the difference in density between the mixo- and monimolimnions is small (Edmondson 1964, Likens and Hasler 1960, Northcote and Hasley 1969, Weimer and Lee 1973). High wind sheltering of these lakes by their surrounding topography has reduced the ability of these lakes to mix and this is thought to have initiated meromixis. As insufficient mixing in these lakes continued through multiple seasons, chemical constituents began to accumulate in the lower strata of the lakes and eventually resulted in them becoming meromictic. These lakes currently exhibit biogenic meromixis, where chemical constituents are cycled from the sediments to the monimolimnion by microorganisms, however, the initiation and maintenance of meromixis is attributed to insufficient wind mixing due to topographic sheltering.

Solar Radiation

The amount of solar radiation interacting with the surface of a waterbody directly impacts its temperature trends and heat budget (Annear and Wells 2007). Variables such as meteorological conditions, shoreline or inflow shading by topography, inflow morphometry and directional orientation (north, south etc.) and littoral zone surface area can all influence solar radiation's effect on both in-lake and inflow temperatures (Annear *et al* 2006, Cole and Wells 2013). The temperature in turn impacts the hydrodynamics, water quality and ultimately biological cycles within the system.

Bathymetry and Basin Morphometry

Bathymetry (topography at depth) and basin morphometry (surface area, average depth, maximum depth etc.) can largely impact the route of water flow, residency time and mixing within an aquatic ecosystem. An example where bathymetry directly impacted changes in mixing and water quality was in Lake Whatcom in Washington, where submerged glacial sills prevented transfer of hypolimnion water between adjacent basins/bays (Pickett and Hood 2008). Periodically, high winds would generate a seiche within this large lake that would push hypolimnion water over these sills, allowing exchange of heat, DO and other water quality parameters between the basins/bays (Pickett and Hood 2008).

It is known that lake dimensions such as surface area, mean depth and volume can influence thermal stratification and heat budgets in lakes (Gorham 1964). Other studies have attempted to investigate the correlation between these lake dimensions and mixolimnion depth in meromictic lakes. Such a correlation would enable predictions of mixolimnion depth change using simple basin dimensions as indicators. When a mixolimnion becomes isothermal and is able to fully mix within itself, there is an exchange of ions, heat etc. across the chemolimnion where the mixo- and monimolimnion meet. This exchange can result in a volume change of these strata where either the mixolimnion forces further turnover and gains volume or the mixolimnion is prevented from deep mixing and the monimolimnion gains volume. This change in volume is accompanied by a change in depth of the mixolimnion, which is an indicator of whether meromictic stability is advancing or deteriorating. Understanding how basin dimensions influence a change in mixolimnion depth can aid in predicting changes in meromictic state over time. The basin morphometry measurements that are strongly correlated with mixolimnion depth are lake surface area and maximum lake depth (Bryhn 2009, McGuire and Currie 1993). One of these studies found other variables including fetch, mean depth, epilimnion depth, mixo- and monimolimnion salinity, difference in mixo- and monimolimnion salinity, elevation and latitude correlated less with mixolimnion depth (McGuire and Currie 1993). Although the data sets in these studies were large and therefore their methods and results having some scientific validity, both studies indicated that their results had limitations and may be too generalized, especially regarding chemical variables. One study completely voided chemical variables (Bryhn 2009) while the other did not consider concentrations in the chemocline, which is the stratum where meromictic stability is increased, maintained or deteriorated. Instead an average salinity was used to represent the entire mixolimnion salinity and the salinity at the lake bottom was used to represent the entire monimolimnion salinity (McGuire and Currie 1993). Making mixolimnion depth predictions based solely on basin dimensions, such as surface area and maximum depth, using underrepresented chemical data could lead to erroneous predictions. These studies also indicated their generality and inability to predict conductivity or salinity directly, which limits precise prediction of meromictic trends (Bryhn 2009, McGuire and Currie 1993). Clearly, chemical variables need also be considered with these predictions and bathymetry/basin morphometry has only a partial influence on lake mixing.

Precipitation, Evaporation, Inflow and Outflow Rate and Water Quality

Precipitation often has low ionic concentrations and can directly dilute both a lake surface as well as the inflowing surface water. Dilution effects by precipitation can readily alter mixing dynamics in meromictic lakes. High inputs of low-salinity precipitation have resulted in reoccurrence of meromixis in lakes with high background salinity that had recovered from past meromictic events. Studies on Mono Lake in California discovered two recent meromictic events separated by 7 years (Jellison *et al* 1998). Meromictic reoccurrence was linked to changes in inflow rate and inflow water quality and demonstrated how previously meromictic lakes that are still saline are sensitive to changes in inflow rate and water chemistry. The study also demonstrated how there is a fine balance between holomixis and meromixis in recovering and previously meromictic lakes (Jellison *et al* 1998, Romero and Melack JM 1996).

Studies performed on Mono Lake, six lakes on Rottnest Island in Western Australia and the Dead Sea in Israel looked at evaporation as being a main process contributing to deterioration of meromixis (Bunn and Edward 1984, Jellison and Melack 1993*b*, Steinhorn 1985). Evaporation of lake surface water can concentrate dissolved constituents thereby causing equalization of salinity between the mixo- and monimolimnion. It should be noted that changes in lake surface elevation due to precipitation, surface inflow and evaporation are connected to the variables discussed above in *Bathymetry and Basin Morphometry* (i.e. change in maximum depth and surface area) (Bryhn 2009, McGuire and Currie 1993).

Calculating Mixing Potential: Preliminary Stability Equations

The initial attempt to understand the dominant processes in lake mixing came from Wilhelm Schmidt's work on developing stability equations (Schmidt 1915, Schmidt 1928). These equations made it possible to calculate the amount of work required by the wind to mix a lake to uniform temperature without the addition or removal of heat (Hutchinson 1957, Schmidt 1915, Schmidt 1928). George Evelyn Hutchinson modified these equations for meromictic lakes allowing calculation of the amount of work required to mix the mixo- and monimolimnion of a meromictic lake if isothermal conditions exist (Hutchinson 1937). The basic theory behind these equations stems from the fact that there are two types of stability that compose total stability (S_T) within a lake and maintain the layers/stratification within the lake: thermal stability (S_t) (due to temperature) and chemical stability (S_c) (due to dissolved solutes) (Ambrosetti and Barbanti 2005). Comparing the magnitudes of S_t and S_c from season to season and year to year is one way of tracking if a lake is evolving towards a meromictic or holomictic state (Ambrosetti and Barbanti 2005). It is interesting to note that for meromictic lakes that have extended periods of thermal stability in summer or winter, the chemocline will be sheltered from mixing action of wind and therefore the fall and spring are the most likely times when changes in meromictic state will occur, when thermal stability is minimal (Walker 1974).

Meromictic Trend Predictions – A Combination of Many Variables

Based on the above review of lake mixing, it is clear that it is a complex process controlled by many mechanisms and variables. Most of the historic studies on meromictic lakes involved some mathematical analysis of observed field data to postulate why meromixis originated and deteriorated and if meromixis has the potential to occur again. Often, only one or a few of the possible variables are analyzed and discussed. Exclusion of one or more variables could result in erroneous predictions, especially if the excluded variable is a dominant controller of lake mixing dynamics and water quality for a particular system. These studies and the data they provide are significant for building limnological knowledge of meromictic lakes. The use of mathematical equations in calculating water mixing has progressed substantially since Schmidt and Hutchinson's stability equations, however; the predictions and conclusions drawn from these studies can be further enhanced by numerical/mathematical inclusion of all variables. Combined efforts of limnologists, chemists, mathematicians, engineers and physicists have resulted in the construction of hydrodynamic and water quality models. These models have been designed to encompass and numerically link together all of the variables discussed above, including topographic shading, heat exchange and shear stresses resulting from water flow drag,; all of which are critical in understanding the hydrodynamics of a system (Patterson *et al* 1984). The magnitude of the effect of these variables on hydrodynamics and water quality changes depending on the system.

Hydrodynamic and Water Quality Modeling

In general, the development of hydrodynamic and water quality models requires conceptualizing and understanding the dominant variables that control water movement and quality in aquatic systems and then developing mathematical equations that link these variables together (Reckhow and Chapra 1983). In order to predict water flow direction and velocity throughout a system, a variety of hydraulic equations have been developed (Chapra 1997, Cole and Wells 2013, Martin and

McCutcheon 1999). Understanding where and at what rate water is flowing through a particular system is critical when trying to make projections about water quality since water is the transport medium for water quality constituents (Reckhow and Chapra 1983). The mathematical complexity of how to predict water flow will only be discussed in simplistic terms here however; many good resources discuss these topics in detail (Chapra 1997, Cole and Wells 2013, Martin and McCutcheon 1999).

Although the topic of modeling has been discussed here as a simplified process of data input, output and calibration/validation; hydrodynamic and water quality modeling set-up and performance is a multi-faceted process that is not always immediately successful depending on the complexity of the system of study. Successful and accurate modeling can only occur if sufficient and appropriate data that encompass the dominant mechanisms acting upon and within the system have been collected and applied to an appropriate model. It is clear that lakes are dynamic systems and although similar variables and properties control water flow and mixing within them, the variables and properties exhibiting the most dominant control can change from lake to lake depending on system specifics. It is impossible to perfectly predict system conditions that will occur in the complexity of the real world however, the use of hydrodynamic and water quality models are the best tools we have available for doing so. Multiple hydrodynamic and water quality models exist, many of which utilize a similar scientific and mathematical framework as discussed below.

Some commonly used hydrodynamic and water quality models include DYRESM (dynamic reservoir simulation model), HSPF (hydrological simulation program), WASP (water quality analysis simulation program), RMA-10 and 11 (resource modeling associates) and EFDC (environmental fluid dynamics code). Some of these are currently managed by the US EPA (United States Environmental Protection Agency). Some of the main characteristics of the various models are dimensionality (1-D, 2-D or 3-D), whether both hydrodynamics and water quality are modeled or if coupling of two models is required, whether sediment diagenesis algorithms are built into the source code and the cost/technical support availability.

There can also be variability in the algorithms used to calculate hydrodynamics and water quality. The model selected by the user must be applicable to the variability and mechanisms within the system to be modeled. For example, if exchange of a certain parameter between the sediment and water column is a main regulator of that parameter in the water column, the model should have some sediment exchange abilities. A variety of good reviews on model types and applications are available (Chapra 1997, Martin and McCutcheon 1999, Reckhow and Chapra 1983).

For the present study, the CE-QUAL-W2 model was utilized and so its specifics will be discussed.

CE-QUAL-W2 Model Input Data

The CE-QUAL-W2 model requires five main categories of data: *geometric data, boundary conditions, initial conditions, hydraulic parameters and kinetic parameters.* The combination of all of this data together can be used to calibrate the model, ultimately allowing for the ability to make future predictions of water quality for the system.

Geometric data is essentially the lake bathymetry, which is used to construct the volume-area-elevation table and the model grid as well as a sufficient portion of topography surrounding the lake to the shoreline (Cole and Wells 2013). CE-QUAL-W2 utilizes a finite-difference grid to simulate the water body. Although a finite difference grid does not conform to the exact dimensions of a system as perfectly as a finite-element grid does, the computational exercises are simpler than with a finite-element model and predictive capabilities are typically not drastically reduced for most systems (Figure II). The mathematical techniques and equation set-ups used by these methods also vary (Mercer and Faust 1980*b*).

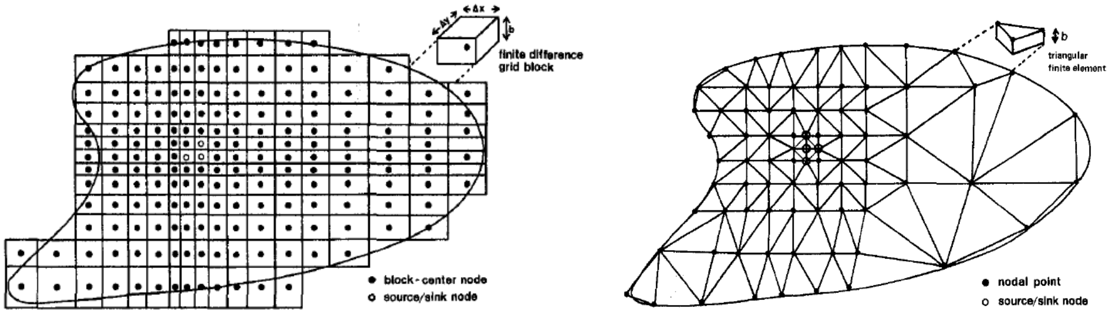
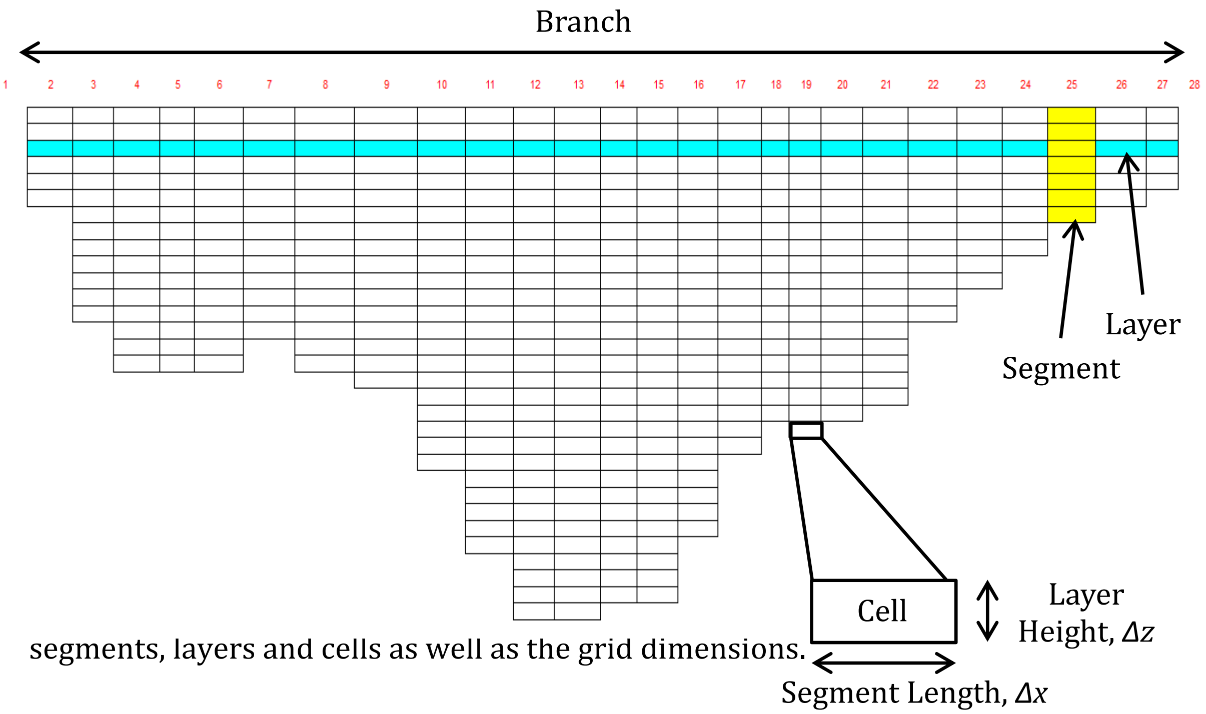


Figure II. Comparison of finite difference and finite element grid set-ups (adapted from Mercer and Faust 1980*a*).

The model grid is the computerized representation of the lake's dimensions and is essentially "how the computer views the lake" in terms of the real-world shape, size and directional orientation.

In CE-QUAL-W2, the finite-difference grid is a series of cells (rectangles) forming horizontal segments and vertical layers (Cole and Wells 2013). In order to give the lake 2-dimensionality, the segments divide the lake into sections from the lake inlet to the lake outlet (horizontally/longitudinally) while the layers divide the lake into sections from surface to bottom (vertically). A side view schematic of a model grid illustrates the layers, segments and cells (Figure III) while a top view illustrates the numbered segments (Figure IV). Inactive (empty) segments are placed at the beginning and end of each branch as shown by the segment numbering scheme in Figure IV. If more complex hydrodynamics and water quality are observed in specific strata within the lake, layer heights can be adjusted to coarsen or fine the grid (Figure V). In CE-QUAL-W2, the grid is composed of either one or more "waterbodies" that are composed of one or more "branches" (Cole and Wells 2013). Branches address variability in bottom slope or shoreline orientation within a system (Figure V) whereas waterbodies address variability in meteorological conditions, water quality or turbulence schemes. The bathymetry file specifies the slope, segment widths, segment angle orientations, layer heights, initial water elevation and bottom sheer stresses for each branch. Bathymetry and surrounding topography can affect water flow patterns and therefore the accuracy of the model grid is critical for proper model calibration.



segments, layers and cells as well as the grid dimensions.

Figure III. Side view schematic of a model grid for single branch including segments, layers and cells as well as the grid dimensions.

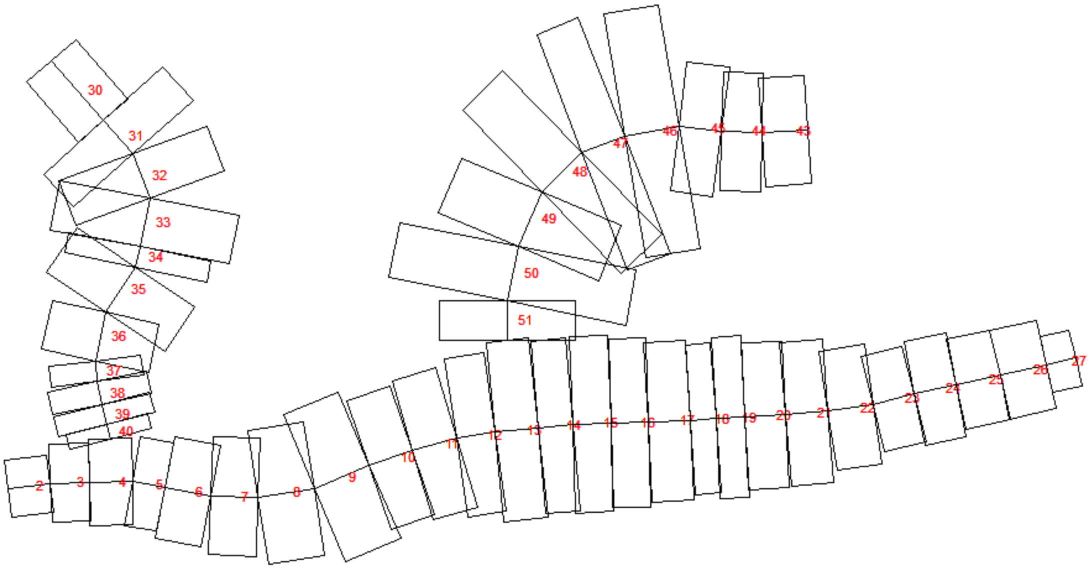


Figure IV. Top view schematic of model grid showing numbered segments.

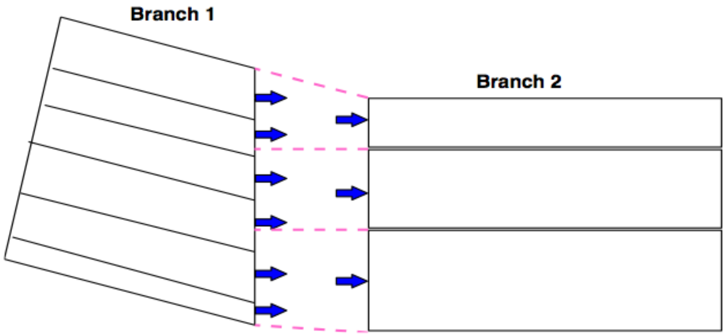


Figure V. Joining of branches to form a complete waterbody. Notice the difference in slope and grid dimensions (layer thickness) between the two branches (Cole and Wells 2013).

Boundary conditions are data that represent the inputs and outputs of momentum, heat and constituents to and from the waterbody at grid boundaries (inflows, outflows, water surface and sediment). In/outflow volumes, temperatures and constituent concentrations, meteorological conditions and precipitation all contribute to the boundary condition representation. Actual momentum, heat and constituents entering the system are accounted for from the in/outflows but the heat exchange due to solar radiation at the water surface, heat exchange with the sediment and the wind's contribution to mixing and momentum are also taken into account both from input data and coefficient adjustment. Once this data has been inputted/adjusted at the boundaries of the grid, it drives the transport of water and constituents through the waterbody system. In order for accurate modeling to occur, consistent monitoring of boundary condition data needs to occur and coefficients need to be an accurate representation of the system.

Initial conditions are data that are used to indicate what physical and chemical variables are present in the waterbody system at the time of model start-up. Once the model simulation has begun, initial conditions are "washed out" of the system domain and replaced by the data inputted at the model grid boundaries. Initial condition variables specified include temperature and constituent concentrations and can be set as isoconditions (whole waterbody is the same), vertically variable (heterogeneous across the layers) or horizontally/longitudinally and vertically variable (each segment and layer is unique) (Cole and Wells 2013).

Hydraulic parameters are related to the hydrodynamic equations of the model. These parameters can be adjusted and dictate how momentum [eddy viscosity (m^2 sec^{-1})] and heat and constituents [eddy diffusivity (m^2 sec^{-1})] are transported both horizontally (dispersion) and vertically (diffusion) through the system domain. The magnitude of bottom friction resulting from flow over the sediment is also dictated by the hydraulic parameters (Cole and Wells 2013).

Kinetic parameters are related more to the water quality equations of the model and there are 120 kinetic coefficients that can be adjusted in the CE-QUAL-W2 model, all related to the rates of processes/reactions influencing constituent cycling such as settling, burial, decay, mortality, excretion, adsorption, respiration, grazing and conversion. Essentially, these parameters control the source-sink relationships within the system domain. Equations are more refined around nitrogen and phosphorus since these constituents are known to have a major effect on phytoplankton, zooplankton, epiphyton and macrophytes. However, any steady-state constituent can be modeled if enough is known about its kinetics (Cole and Wells 2013).

Model Calibration

Calibration data is essentially field data from known locations and dates within the waterbody to compare with the model outputs/predictions. This is the point where boundary condition data and calibration data come together to confirm whether the model is accurately predicting the hydrodynamics and water quality concentrations for the waterbody. By only providing the model with initial condition data from within the model domain/grid (in-lake data) on Day 1 of the simulation and giving it no further in-lake data, it requires the model to only use the boundary condition data for computations within the system. Since boundary condition data is truly what drives the model, this data should be as comprehensive and well-characterized as possible for an effective model. Having a large data set of calibration data (in-lake) will not be useful if what is entering and leaving the system is not well known.

Model equations contain many coefficients that sometimes are not suited to certain systems and must be adjusted so that they properly represent the conditions of a specific system. One very commonly adjusted parameter is the wind-sheltering coefficient (wsc). In the CE-QUAL-W2 model, this coefficient ranges from 0.3 to 0.9 and is used as a multiplier for wind speed data, ultimately reducing the effect of the wind speed on the lake. Often, meteorological data acquired for modeling is obtained by meteorological stations that are not present on the study lake shore but in a more open area (i.e. airport). Therefore, most meteorological stations are not capturing wind speeds representative of actual wind speeds present on the lake surface where wind-sheltering by topography or vegetation has occurred. For this reason, most wind speed data is often higher than the actual wind speeds present at the lake surface and so adjustment of the wind-sheltering coefficient is required. Large deviations in model results can occur if this value is not correct since the input/output of heat and input of momentum to/from the lake surface is largely impacted by wind. Multiple model runs and adjustments are typically necessary before a model can be deemed properly calibrated. Model calibration and validation are performed simultaneously. Once a model run is completed, absolute mean errors (AME) are calculated for the comparison of calibration data with model output data. It is up to the modeler what they accept as an appropriate AME for a specific parameter however the AME should be as small as possible. For example, AME<1.0°C is a common goal for temperature calibration. A variety of error reporting strategies have been used for to interpret CE-QUAL-W2 outputs however, the AME has proven to be the most useful. As a direct quote from the CE-QUAL-W2 manual, "… the AME provides the best indication of model performance since it is directly interpretable. For example, an AME of 0.5°C means that the model results are, on the average, within 0.5°C of the observed data" (Cole and Wells 2013). The AME calculation is shown below:

$$\mathbf{AME} = \frac{\sum |\,\mathbf{Predicted} - \mathbf{Observed}\,|}{\mathbf{Number\ of\ observations}}$$

CE-QUAL-W2 – Transport Scheme

The main equations encompassed in most hydrodynamic models, including CE-QUAL-W2, are based around laws of conservation of energy, momentum and mass and allow the model to transport a fluid phase about a control volume (model domain/grid) (Cole and Wells 2013, Martin and McCutcheon 1999). Equations ultimately calculate sheer stresses in the x, y and z-directions (horizontal/longitudinal, lateral and vertical respectively) (Figure VI). Sheer stresses do not only occur between flowing water and the bottom/shoreline, they also occur between layers or columns of water flowing within the waterbody. Simply put, at the boundary of two flowing water strata (layers), the two layers still inflict sheer stresses on each other and so calculations for this occur throughout the entire model grid. A continuity equation links all of the sheer stresses and ultimately, velocities together.

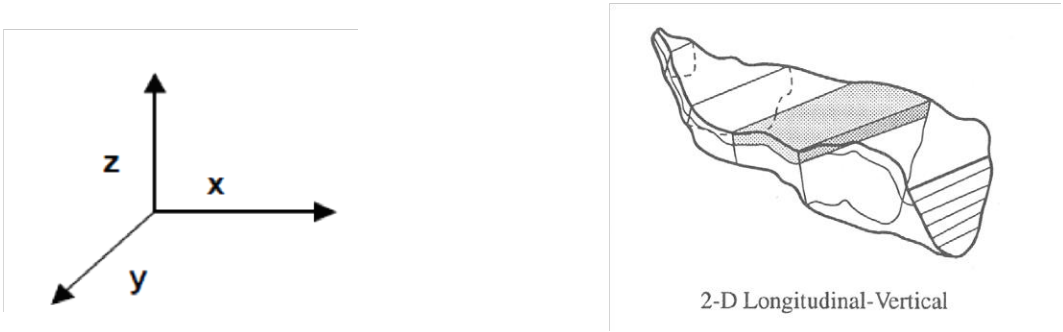
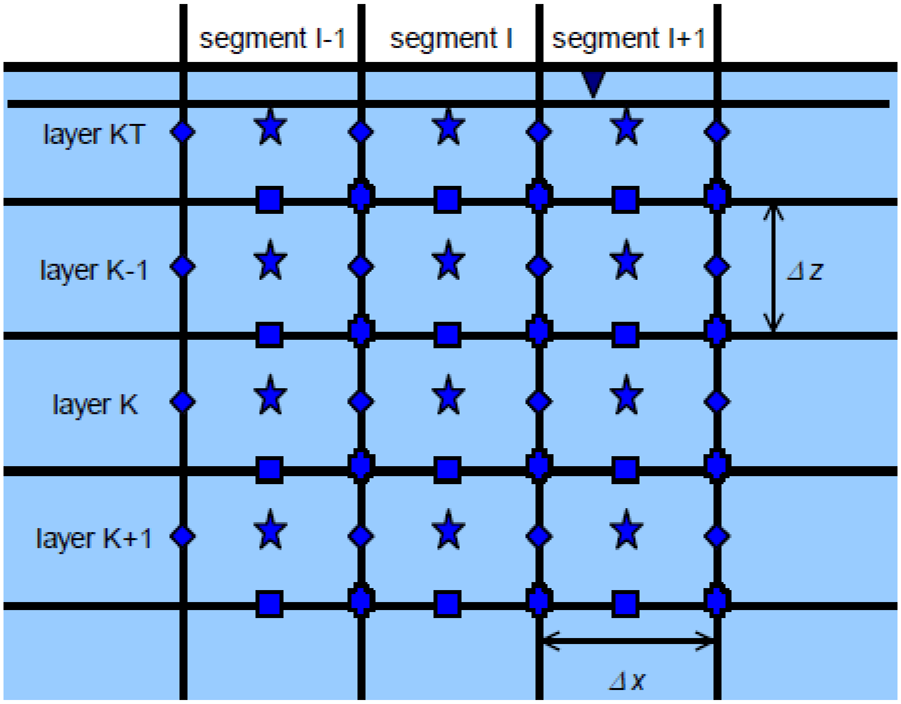


Figure VI. Directionality in a model domain (modified from Martin and McCutcheon 1999).

CE-QUAL-W2 is a laterally-averaged model meaning that its equations are designed such that all variables in the lateral (*y*-direction) are assumed to be constant within the system. The premise behind modeling in 2-dimensions and averaging the third is that the computational requirements of the model are lessened and simplified. For many aquatic systems, 3D-variablity in flow, heat and water quality is not so great that 3D-modeling is required and often, 2D-modeling is sufficient. For CE-QUAL-W2, all transport equations in the y-direction are averaged (Figure VI).

Eddy viscosity and diffusivity are the transport of momentum and heat/water quality constituents respectively. Since density influences fluid flow, the equation of state is also incorporated in these models and it relates fluid density to temperature and dissolved substances in the system.

The model grid (discussed previously) represents the domain where the hydrodynamic and water quality equations perform calculations to transport momentum and heat/constituents through the system. Figure VII displays the locations in the grid where specific variables are defined and calculated in space. Any particular cell in the model grid is located at layer *K*, segment *I*.



◆ Horizontal velocity, longitudinal eddy viscosity and diffusivity, internal sheer stress
★ Pressure, average cell width, density, temperature, constituent concentration
■ Vertical velocity, vertical eddy diffusivity
● Vertical eddy viscosity

Figure VII. Locations of various parameter transport equations. Any particular cell (K, I) is denoted by layer "*K*" and segment "*I*" (Modified from Cole and Wells 2013).

As data is provided to the model via boundary condition input files, the model inputs the data into the hydraulic and water quality equations at the respective locations in the grid. The results of calculations at a cell (*K*, *I*) are used to perform calculations at cell (*K*+1, *I*+1) downstream in the grid (Figure VIII). This process continues iteratively both horizontally and vertically though the model grid. The opposite can also occur if negative flow conditions occur in the waterbody (Figure IX).

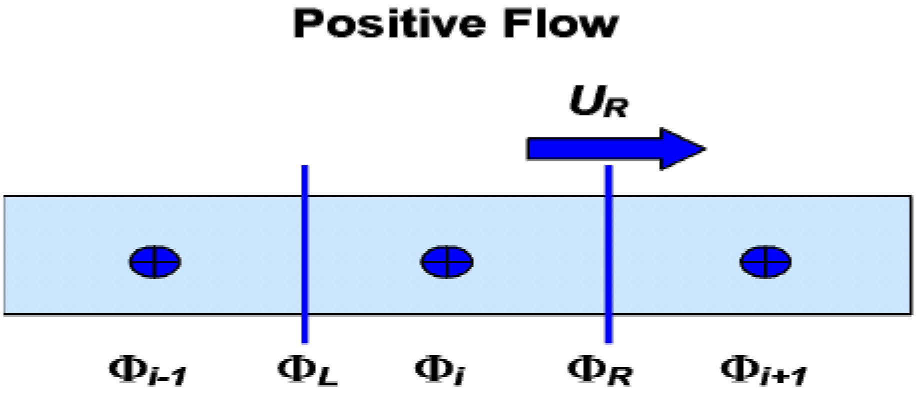


Figure VIII. Schematic of positive horizontal flow velocity from cell (*K*, *I*) to cell (*K*+1, *I*+1) (Modified from Cole and Wells 2013).

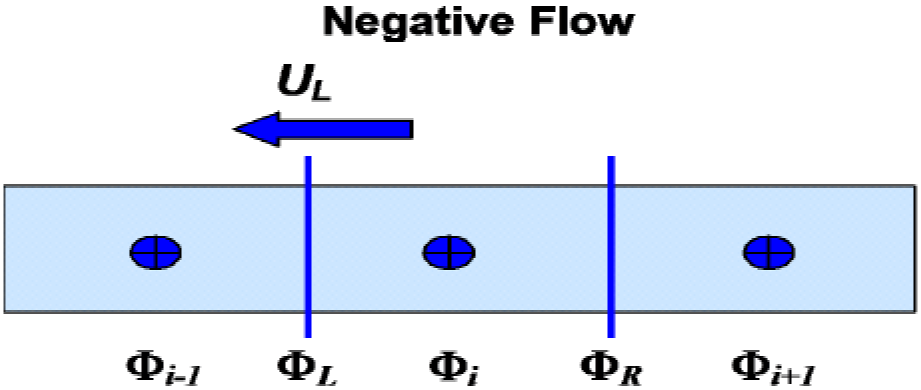


Figure IX. Schematic of negative horizontal flow velocity from cell (*K*, *I*) to cell (*K*-1, *I*-1) (Modified from Cole and Wells 2013).

To perform all of the calculations for hydrodynamics and water quality, CE-QUAL-W2 uses the ULTIMATE-QUICKEST computation scheme (Leonard 1979). This computational scheme works to minimize numerical diffusion that can occur at areas of strong gradients where data variability can be large from grid cell to grid cell. The ULTIMATE computation scheme allows for the ability of data at 3 nodes to be used to solve equations at any one cell (Leonard 1979). To perform a calculation at a cell, data from the node of the upstream cell as well as data from two other nodes of cells in a single, coordinate direction are used (Leonard 1979). The QUICKEST portion of the computation scheme works to minimize over or underestimations of data that tend to occur at the trailing edge of a sharp gradient if only the ULTIMATE formulations are used (Leonard 1991).

Limitations and Assumptions of CE-QUAL-W2

The model manual (Cole and Wells 2013) outlines the main limitations and assumptions of the model. The two-dimensionality of CE-QUAL-W2 is one of its main assumptions. Again, this means that all momentum, heat and constituents are assumed to be the same in the lateral (z) direction/dimension. Currently, the Boussinesq and hydrostatic approximations are used regarding the vertical turbulence schemes. Essentially this means that the model may have difficulty predicting vertical accelerations if they are present. CE-QUAL-W2 does not have a sediment diagenesis component currently meaning it does not have the ability to model complex kinetic exchanges between the sediment and water column. Only first order, temperature-controlled reactions are possible to model using an Arrhenius multiplier. As already discussed, the transport schemes included in the model have a component of limitation as well. The ULTIMATE method should be used because it makes up for both the numerical stability that can occur from the UPWIND scheme and the over and under predictions that can occur from the QUICKEST scheme if gradients of variability are appreciable.

Chemical Cycling in Meromictic Lakes: An Overview

There are some key distinctions in chemical composition between seasonally anoxic or meromictic lakes and holomictic lakes, much of which can be attributed to increase in ion and metal concentrations with depth and decrease in redox potential with depth from prolonged anoxic conditions (Hongve 1997). The prolonged absence of oxygen in the monimolimnion of a meromictic lake is unique and alters the oxidation states of many constituents such as sulphur (S), iron (Fe), manganese (Mn), magnesium (Mg) nitrogen (N), copper (Cu) and zinc (Zn).

Sulphur Compounds

Sulphur is typically not a limiting nutrient in aquatic systems for phytoplankton due to its abundance and it is typically required by species at a similar concentration to phosphorus (Lehman and Branstrator 1994, Urban *et al* 2001). The chemical form of sulphur in aquatic systems is controlled either directly or indirectly by many factors including oxygen content (Davison and Heaney 1978, Hem 1960*b*), pH, Eh (Hem 1960*b*, Hem and Cropper 1959, Hem and Skougstad 1960), other chemical constituents present in the system (Hem 1960*a*,*b*) and microbiological activity (Jørgenson 1979, Rudd *et al* 1986). Although sulphur typically takes an anionic form, the oxidation state of sulphur can range from S^{2-} to S^{6+}, which further increases the possible chemical species it can form (Hem 1960*b*). Sulphate (SO_4^{2-}), bisulphate (HSO_4^-), thiosulphate ($S_2O_3^{2-}$), sulphide (S^{2-}), and metallic sulphides (MeS where Me = Cu, Fe, Zn etc.) are common forms that sulphur takes during its lake cycle (Hem 1960*b*, Jørgenson 1990). Sulphate salts that contain Na^+, K^+, Mg^{2+} etc. typically do not precipitate until the lake is supersaturated and therefore these salts can become highly concentrated in meromictic lakes (Hongve 1980). These salts can precipitate during evaporation at the surface of the lake. It is also possible that co-precipitation of these ions on settling organic molecules can occur. In anoxic conditions, sulphur reduction converts SO_4^{2-} to S^{2-} or HS^{2-} in high pH or SO_4^{2-} to H_2S in acidic/neutral waters (Cook 1982, Hem 1960*b*, Urban *et al* 2001). Sulphite and thiosulphate are known intermediates of sulphide oxidation/reduction and they can be either reduced back into sulphide or oxidized into sulphate (Hem 1960*b*, Jørgenson 1990, Rudd *et al* 1986). H_2S persists in acidic conditions but its presence can be removed by metals such as Fe, which will form FeS or FeS_2 precipitates (Hem 1960*b*). Organic sulphur is a dominant form of sulphur in lake systems and is abundant in lake sediments (Kling *et al* 1991, Rudd *et al* 1986). In sediment pore waters, sulphates will convert to sulphides and can form organic sulphur. This has been shown to be a dominant removal mechanism of sulphur from the water column (Rudd *et al* 1986). Organic sulphur has been found to be dominant fate of reduced sulphur in lake sediments (Kling *et* al 1991, Nriagu and Soon 1985, Rudd *et al* 1986), however, sulphides have also been found to comprise a significant proportion of sediment total sulphur (Carignan and Tessier 1988, Giblin *et al* 1990). During lake turnover, both sulphides and organic sulphur forms, can be oxidized to sulphate, although sulphide oxidation is typically favoured (Kling *et* al 1991, Nriagu and Soon 1985, Rudd *et al* 1986). Understanding the main chemical pathways of sulphur in lake systems is important in trying to understand the long term fate of sulphur in meromictic lakes and how this links to lake remediation.

Iron and Manganese

When not bonded with organic molecules or metals, iron predominantly forms either soluble or insoluble oxides, hydroxides or carbonate molecules (Hongve 1980, Hongve 1997). Oxidized iron (Fe^{3+}) (ferric) is relatively insoluble compared to reduced iron (Fe^{2+}) (ferrous) however both forms precipitate in their hydroxide forms ($Fe(OH)_2$ and $Fe(OH)_3$) (Hongve 1980, Hongve 1997). Fe^{3+} is the more stable form during oxic conditions while Fe^{2+} predominates during anoxic conditions (Mortimer 1941). During anoxic conditions it is common for dissolved Fe concentrations to increase in the water column (Hamilton-Taylor *et al* 1996, Hongve 1997, Mortimer 1941). This process intensifies when DO drops to <1 mg L^{-1} (Mortimer 1941). When anoxic conditions occur in the water column, the Fe contained in the sediment as insoluble ferric compounds can be reduced to its more soluble ferrous form allowing it to be readily mobilized from the sediment to the water column (Mortimer 1941). This process will continue to occur until oxic conditions return. During turnover, Fe is oxidized and precipitated back again to the sediments (Hamilton-Taylor *et al* 1996, Mortimer 1941). During anoxia, solubilized Fe in the hypolimnion that approaches the oxic epilimnion via eddy diffusion is readily oxidized and descends back into the anoxic hypolimnion (Mortimer 1941, Shaked *et al* 2002). It is also possible for the opposite to occur where Fe becomes insoluble and is removed from the water column. This occurs as a result of FeS or FeS_2 formation in high-sulphur lakes (Davison and Heaney 1978). Fe^{2+} also readily complexes with organic compounds such as tannic acid (Hem 1960*a*). This stable complex does not prevent typical redox-controlled cycling of Fe between ferrous and ferric forms but it can slow this process, keeping Fe^{2+} dissolved, even in anoxic conditions (Hem 1960*a*).

Congruent redox cycling occurs with Mn but with some differences. The redox potential of Mn is greater than that of Fe meaning its oxidation occurs at a slower rate/reduction at a faster rate (Davison 1993, Hongve 1997). Thus, Mn remains reduced and therefore dissolved in the water column longer during turnover than rapidly oxidizing Fe does (Davison 1993, Hongve 1980, Hongve 1997). The source of elevated Mn concentrations in anoxic depths of lakes has thus been linked to dissolution and sinking of Mn slowly oxidized from the epilimnion rather than exclusive solubilized Mn from the sediment (Balistrieri *et al* 1992, Davison 1981, Davison *et al* 1982). However, Mn can still be sourced from the sediment and Mn that rises from anoxic bottom waters and enters oxic surface waters may not be immediately oxidized/precipitated and therefore has the potential to rise higher into the water column and get transported through the outlet of the lake (Davison *et al* 1982). Although MnS formation is possible in anoxic bottom waters, it is usually not favoured due to Mn levels typically being lower than those necessary for precipitation (Balistrieri *et al* 1992).

Zinc and Copper

Zn and Cu dynamics can differ and be more complex than that of Fe and Mn. Phytoplankton can readily harvest these micronutrients and release them during decay (Riley 1939, Hamilton-Taylor *et al* 1996). Zn and Cu concentrations tend to be lower in anoxic conditions at a lake bottom due to precipitation as ZnS and CuS (Hamilton-Taylor *et al* 1996). Cu also readily adsorbs onto organic matter, which can act as an alternative removal mechanism (Riley 1939). Zn and Cu, similar to Fe and Mn, typically form insoluble compounds in oxic conditions. For all of these reasons, Cu and Zn typically are more elevated closer to lake surfaces during stratification rather than near bottom.

Nitrogen

The common forms of nitrogen found in aquatic systems include dissolved N_2, ammonia (NH_4^+), organic nitrogen (proteins etc.), nitrite (NO_2^-) and nitrate (NO_3^-) (Keeney 1973). Reduction of dissolved nitrogen to ammonia is known as nitrogen fixation and is performed by heterocyst cells in nitrogen-fixing cyanobacteria bacteria and other capable photosynthetic bacteria (Keeney 1973). It is interesting to note that the molybdenum:sulphate ratio can control the activity of nitrogen-fixing cyanobacteria (Howarth and Cole 1985, Marion *et* al 1990). Sulphate acts as an inhibitor to nitrogen fixation enzymes since it similar to the molybdate ion, which is essential for proper function of the enzymes required for nitrogen fixation (Howarth and Cole 1985, Marino *et al* 1990). Ammonia created from nitrogen fixation is either directly or indirectly assimilated into aquatic organisms (bacteria, phyto- and zooplankton, macrophytes, invertebrates, fishes etc.) and becomes organic nitrogen (Keeney 1973). The indirect pathway first involves nitrification, which is oxidation of ammonia into nitrite and subsequently to nitrate, which is then assimilated into organic nitrogen (Keeney 1973. When organisms die and decay, the organic nitrogen is converted to ammonia once again by bacteria in a process known as ammonification (Keeney 1973). Some nitrogen may not undergo this process and can be stored long-term in the sediments in a process known as sedimentation (Keeney 1973). Ammonia developed from ammonification can be once again directly assimilated into organic molecules within organisms or it can undergo nitrification to form nitrate, which is highly soluble and also biologically available for re-incorporation into organic forms (Keeney 1973). The processes of sedimentation, ammonification and nitrification at the sediment-water interface are dominant when dictating the fate and form of nitrogen present in an aquatic system. Dissolved oxygen concentration, temperature, pH and temperature are variables that can affect which nitrogen-conversion pathway will be favoured (Keeney 1973).

Meromictic events can alter the nitrogen cycle within a lake, particularly at the sediment-water interface. The nitrogen cycle can begin to resemble summer conditions in a eutrophic lake since both have low dissolved oxygen levels in their lower strata (Keeney 1973). During meromixis, decaying organic nitrogen will predominantly undergo ammonification and increase NH_4^+ levels within lower strata (Keeney 1973). The absence of full water column turnover in the spring and fall eliminates the vertical transport of NH_4^+ from lower to upper strata and this further accumulates NH_4^+ in the monimolimnion and depletes it in the mixolimnion (Jellison *et al* 1993). The 6-year meromictic event in Mono Lake, CA showed all of these trends (Jellison *et al* 1993). With high volumes of ammonia being contained to the monimolimnion, decreases in algal photosynthesis were observed in the mixolimnion (Jellison *et al* 1993). When meromixis deteriorated, upward vertical flux of the monimiolimnion-stored ammonia cause great increases in the mixolimnion, although a great deal of the nitrogen was lost to the atmosphere as N_2 (Jellison *et al* 1993). The concentrations of nitrogenous compounds contribute to the overall TDS and chemical stability in a meromictic lake and so having an understanding of nitrogen mechanisms in a system is important. Since nitrogen is a critical nutrient for biota of all trophic levels, changes in populations as a result of meromixis can be partially inferred from the form and concentration of nitrogen in the system.

Chlorophyll a

Chlorophyll *a* (chl *a*) is commonly used as an indicator of phytoplankton biomass in aquatic systems (Lorenzen 1966, Osmund *et al* 1965). There are many variables that affect chl *a* correlation with phytoplankton biomass and often, a direct correlation is not possible (Cullen 1982, Lorenzen 1965). Phaeophytin *a*, which is chl *a* minus its magnesium ion, can also be measured by both fluorescence and laboratory measurement methods of chl *a* and if possible, subtraction of phaeophytin concentrations from chl *a* concentrations should occur (Cullen 1982, Lorenzen 1965, Lorenzen 1966, Osmund *et al* 1965). In a similar way, chl *a* from dead phytoplankton can also contribute to concentrations measured by these methods, resulting in an over-estimation of phytoplankton biomass (Cullen 1982, Lorenzen 1965). The sinking of the perished phytoplankton often results in a "chlorophyll maxima" at depth that is not always an accurate representation of live, viable phytoplankton (Cullen 1982, Lorenzen 1965). As well, adaptability of various species to specific habitats can influence chl *a* and biomass comparisons. Species adapted to low light conditions in more nutrient-rich bottom waters have been found to produce higher chl *a* concentrations to survive compared to high-light, low nutrient surface waters (Cullen 1982). Rapid production of chl *a* can also occur by some species if they are taken from a high-light environment and placed in a low-light environment (Cullen 1982). Such experiments are a testament to the complexity of phytoplankton dynamics and how thought should be put into interpreting chl *a* data.

Silica

It is common for Si to increase in concentration in anoxic waters resulting from its release from sediment (Mortimer 1941). Ferri-silico-humate is a complex in the sediment and it contains Si and Fe. Its destruction during reducing conditions is a main source of dissolved Si (and Fe) into the water column (Mir and Kachroo 1982, Mortimer 1941). Oxic conditions can reform the complex, causing Si and Fe precipitation. Si dynamics also follow closely with phytoplankton growth, particularly the diatoms, which incorporate Si into their frustules. Measurable depreciation of Si can occur in surface waters if phytoplankton growth is productive (Mir and Kachroo 1982, Mortimer 1941, Munawar and Munawar 1975).

Meromixis and Lake Biodiversity

Multiple habitats are present within meromictic lakes since both anoxic and oxic sediment and water are present for an extended period of time. The added variation of pH, dissolved solids concentrations and the redox state of chemical species (sulphur, nitrogen etc.) further increase the habitat structure within the system. The multitude of habitats present can have a high level of biodiversity, hosting organisms able to survive in each particular environment.

Meromictic Lake Cadagno in Switzerland has a variety of phototrophic sulphur bacteria within its 11.5 m - 14 m chemocline (Tonolla *et al* 1999). Species requiring more light and oxygen but utilizing the higher nutrient levels for growth were found near the chemocline surface whereas species more tolerate of high sulphide were present towards the chemocline bottom (Tonolla *et al* 1999). In addition, sulphur-reducing and sulphur-oxidizing bacteria have shown a source-sink relationship in sulphur conversion within the chemocline (Tonolla *et al* 2004). A shift in dominance of purple sulphur bacteria to green sulphur bacteria occurred in this lake and it was linked to a potential mixing event during that year that would have altered conditions within the lake (Tonolla *et al* 2005). This has been observed in other lakes as well (Jorgensen *et al* 1979).

A unique relationship between phytoplankton and purple sulphur photosynthetic bacteria was observed in meromictic Big Soda Lake, Nevada (Cloern *et al* 1983). Nutrient levels in the epilimnion strata were too low during summer thermal stratification to support phytoplankton growth however the clearness of the water allowed enough light passage such that the bacteria were able to flourish in the hypolimnion where nutrients were more plentiful. During winter turnover (non-ice forming lake), nutrients from the hypolimnion entered the epilimnion and allowed dense populations of diatoms to develop. This ultimately decreased the populations of the bacteria below due to the reduced light extinction into the hypolimnetic strata. Nitrogen accumulation in the monimolimnion of Mono Lake, NV reduced phytoplankton growth in the lake during the period of meromixis and as the meromictic stability in the lake began to deteriorate, ammonium allocation into upper strata allowed phytoplankton to flourish once again (Jellison and Melack 1993*a*). Antarctic meromictic lakes are especially unique environments due to extreme temperatures and light conditions (Laybourn-Parry *et al* 2002). As a common trend, only a small number of species have evolved to survive and thrive in such extreme environments (Laybourn-Parry *et al* 2002).

The distribution of macrophytes in the littoral zone is controlled largely by the optimal temperature, light, inorganic carbon availability and sediment composition (Barko *et al* 1996). Even though most macrophytes (aquatic plants) present in effluent-receiving lakes are rooted in littoral mixolimnion strata above the chemocline, macrophytes can still be affected by the availability or toxicity of nutrients in the water column and sediment. Macrophytes are able to adapt to changes in their environment such as alterations in water levels from year-to-year (Leck and Brock 2000) and halophytes are able to live in high-salinity environments (Nielsen *et al* 2003). Macrophytes able to survive rapidly-changing or extreme conditions have evolved either a tolerance or strategy to recognize and respond to the change. This ability to survive has been part of the evolutionary history of these plants and rapid environmental changes, such as salinity, can negatively impact macrophytes, such as inhibiting seed germination (Nielsen *et al* 2003).

Unlike plants, fish can be affected by the anoxic conditions in the lake bottom since it decreases their habitat range. Fish have a variety of behaviors that will allow them to cope with decreased oxygen levels and minimize energy use (Kramer 1987). Air breathing, aquatic surface respiration or habitat relocation are common strategies utilized (Kramer 1987). Yellow perch (*Perca flavecens*) have demonstrated decreased food consumption at around 3.5 mg L^{-1} and growth reduction at 2 mg L^{-1} dissolved oxygen (Carlson *et al* 2011). Northern pike (*Esox lucius*) prefer shallower, warmer waters (Casselman and Lewis 1996) and could likely survive in the mixolimnion. However, loss of macrophytes in near-shore areas that serve as breeding and nursing areas for *E. lucius* as a result of effluent discharge (discussed earlier) can negatively impact *E. lucius* populations (Casselman and Lewis 1996). In addition, if sediment porewaters are high in hydrogen sulphide, sac fry growth and survival is greatly reduced (Casselman and Lewis 1996). *E. lucius* juveniles are more tolerant of lower oxygen than adults (Casselman and Lewis 1996).

As a whole, organisms are able to adapt to new conditions in their environment and can develop tolerance. If their environment changes too rapidly though, aquatic organisms typically cannot adapt quick enough and populations and system biodiversity can be negatively impacted. When effluent discharge into a freshwater system occurs, changes in salinity, development of meromixis and change in dissolved oxygen will ultimately follow in most cases. Organisms of these freshwater systems have evolved in a low-salinity, high-oxygen environment, and the changes caused by effluent discharge are often too rapid for these organisms to adapt. Organisms can be either lost from the system or have their growth and fecundity reduced as a result.

CHAPTER 1 – Water Quality and Meromictic State of Study Lakes

Introduction

Mining Effluent Water Quality Regulations

Tailings water from gold mining operations is managed and treated until its quality is within the Federal (Metal Mining Effluent Regulations) and Provincial (Municipal Industrial Strategy of Abatement) limits as well as the Certificate of Approval (COA)/Environmental Compliance Approval (ECA) that has been developed for the operation (Environmental Protection Act 2007, Ministry of the Environment 1999, Minister of Justice 2015). Provincial Water Quality Objectives (PWQO) (Ministry of the Environment and Energy 1994) and/or Site Specific Water Quality Objectives (SSWQO) are also used to guide operations towards acceptable water quality of their discharged effluent. Water that meets compliant levels of heavy metals, ammonia, cyanide, pH etc. and continually passes acute and chronic toxicity tests is discharged to a natural surface water environment. This is the common practice used for most metal mine environmental management strategies. Some elements typically not governed by the above regulations include Ca^{2+}, Cl^-, Na^+, K^+ and SO_4^{2-}. These ions are discharged at elevated concentrations into freshwater receiving environments and therefore, both historic and current mining operations are often associated with lakes having elevated salinity, which can lead to meromictic conditions.

Natural Meromictic Lakes in Ontario

Ontario has very few documented, naturally occurring meromictic lakes (Anderson *et al.* 1985). Since most lakes in Ontario have low salinity, a majority of Ontario's natural meromictic lakes have resulted from unique water quality in combination with lake morphometry and wind sheltering. A prime example of this is Sunfish Lake near Waterloo, ON, which demonstrates biogenic meromixis (Duthie and Carter 1970).

Of the 58 lakes studied in the Experimental Lakes Area (ELA) near Kenora, ON, four lakes are meromictic (Schindler 1971). Two of these lakes (Lakes 120 and 241) were meromictic prior to being used for field experiments and have remained meromictic throughout experimentation years (Brunskill *et al* 1971, Campbell 1977, Campbell and Torgersen 1980, Rudd *et al* 1941). The other two lakes (Lakes 227 and 230) were turned meromictic due to the introduction of nitrogen and phosphorus for eutrophication experiments (Cook 1984, Johnson and Vallentyne 1971, Rudd *et al* 1941, Schindler 1980).

Mine-Influenced Meromictic Lakes in Ontario

Although Ontario has a long history of mining, very few primary/peer-reviewed studies on the lakes receiving discharged effluent from these mining operations are available. Except for a select few lakes that have been studied, the presence of meromixis in these mine effluent-receiving lakes is largely unknown. At the now-decommissioned Winston Lake Mine near Schreiber, ON (owned by INMET Mining Corporation (First Quantum Minerals Limited)), two meromictic lakes have been studied. Copper and iron mining occurred here from 1988 to 1999 and meromictic conditions persisted in Cleaver and Horneblende Lakes downstream of the mine as a result of receiving high-salinity effluent (Denhom *et al* 1995, Haapa-aho 2003). Studies on Cleaver and Horneblende Lakes from October 1999 – March 2001 found that Cleaver still remained meromictic whereas Horneblende had returned to being holomictic once again (Haapa-aho 2003).

Near Atikokan, ON, Steep Rock Iron Mines Limited and Caland Ore Limited operated the Hogarth and Caland pits. Open-pit iron mining occurred from 1944 to 1979 and the pits were allowed to flood after production ceased (McNaughton and Lee 2010). A variety of limnological and geochemical studies have been performed on these pit lakes (Godwin 2012, McNaughton and Lee 2010, Mikkelsen 2012). Both pits are meromictic (Godwin 2012, McNaughton and Lee 2010) and expected to overflow in the next 65-72 years as predicted using hydrodynamic modeling (Mikkelsen 2012). The utilization of the Caland Pit for aquaculture of chinook salmon and rainbow trout is an example of practical usage of a mine-impacted aquatic ecosystem (McNaughton and Lee 2010).

Also in northern Ontario is the meromictic Mattabi Crown Pillar Pit Lake near Ignace (Brassard *et al* 1996). Research on the Crown Pillar Pit Lake showed that it was a promising site for disposal of acid-generating tailings in its anoxic strata

(Brassard *et al* 1996). Keeping the tailings in an anoxic environment would minimize acid-generation from the tailings. Lakes near salt mining operations are also at risk of becoming meromictic due to effluent discharge or spills. One such example is Lake Hallstättersee in Austria which continually receives saline wastewater and was downstream of two large brine spills (Ficker *et al* 2011). Lake Hallstättersee alternates between holo- and meromixis.

Although not in Ontario, Kennady Lake in the NWT is an example of a system where meromixis is expected to occur as a result of diamond mining planned to start in 2016 at the De Beers Gahcho Kué Project (Vandenberg *et al* 2015). Kennady Lake is expected to develop meromictic stability, especially after mine closure, and maintaining this meromixis in Kennady Lake is the current post-closure strategy (Herrell *et al* 2015). Maintaining meromixis in Kennady Lake will ensure that saline water accumulated from site run-off, groundwater inputs, pit dewatering and effluent discharge will be kept isolated from the overlying low salinity water which will be allowed to flow through the system and therefore downstream watersheds will be less impacted (Herrell *et al* 2015, Vandenberg *et al* 2015). This strategy has been utilized successfully in the past at other Canadian mine operations (Brassard *et al* 1996, Fisher and Lawrence 2006, Hamblin *et al* 1999).

Meromixis in Lim and Frank Lakes

In the present study, I examined water quality in two mine influenced lakes, Lim Lake and Frank Lake, had their current water quality examined. Alterations of multiple water quality parameters have occurred in Lim and Frank Lakes as a result of receiving effluent from the Hemlo operation (Tables 1.1 and 1.2, Appendix B). Baseline studies were conducted for Lim and Frank Lakes in 1983 (Wood 1984) and 1984 (SENES Consultants Limited 1984) respectively. Lim Lake received treated effluent from Golden Giant Mine from 1985-2006 and from David Bell Mine from 1986-1999 (Beak International Incorporated 2000*d*), while Frank Lake has been receiving effluent from David Bell and Williams since 1999 and 1987 respectively and will continue to until mining ceases at Williams (Beak International Incorporated 2000*a*, Orr and Stecko 2006*b*).

Despite water quality improvements in Lim Lake that occurred in the two years after discharge cessation, natural dilution of the surface strata of Lim Lake resulted in the meromictic conditions being established (Weech and Orr 2009*a*). Lim Lake first exhibited meromixis after early ice-on in fall 2008 and this incomplete turnover persisted into spring 2009 (Weech and Orr 2009*a*). Turnover only occurred down to 6-7 m during these seasons (max lake depth = 12 m). A profile taken during fall 2009 also indicated persistence of meromictic stability in the lake from 8m to the bottom (unpublished data).

Frank Lake first began showing some meromictic stability in September 1992 since constant temperature was observed down to 19m but specific conductance (sp-cond) and DO demonstrated the presence of a monimolimnion (ESP 1993). Chemical stability was apparent but to a lesser degree during the fall 2009 EEM (Beak International Incorporated 2000*a*). The first documented mention of meromixis in Frank Lake occurred in the 2008 EEM where a definite chemocline between 5 m - 6 m and anoxic conditions were observed at 5 m (Orr and Stecko 2009*b*). It is possible that the chemocline had already been established in 2005 but only conductivity (not specific conductance) was reported in the 2005 EEM so interpretation is difficult (Orr and Stecko 2006*b*). Data measured in November 2010 (after fall turnover) by Hemlo staff showed a chemocline between 10m and 12m, indicating that meromixis was still present in Frank Lake (unpublished data).

Objectives

The objectives of the current study's first chapter were to:

1) Perform a comprehensive water quality study of both Lim and Frank Lakes and relate the water quality, particularly sulphur, to the meromictic stability in the study lakes.
2) Use water quality at the time of turnover (spring and fall) to compare the meromictic states of Lim and Frank Lakes and whether stability is deteriorating or strengthening over the study duration and relate this to the lakes' management strategies.

3) Identify which parameter(s) could be used to develop a model that could predict meromictic stability trends in Frank Lake, which is currently receiving effluent discharge.

Hypotheses

At the time of commencing this study (2011), it had been three years since an in-depth water quality study had been performed on the lakes. It was therefore important to monitor and assess the current water quality and meromictic state of both lakes. Based on past literature on mine-impacted meromictic lakes such as Cleaver Lake and the past consultant studies on Lim and Frank Lakes, it was hypothesized that both Lim and Frank Lakes were still meromictic due to a short natural remediation time (Lim Lake) and current effluent discharge receiving (Frank Lake).

Sulphur is one of the highest concentrated anions and salt components in both lakes and so initially it was selected as the parameter acting as a proxy for predicting mixing trends and focal parameter for modeling.

Methods

Study Site

Location

The Hemlo Gold Mine property operated by Barrick Gold (Figure 1.1, Appendix A) is the site of two lakes, Frank Lake (48.65 lat, -85.84 lon) and Lim Lake (48.40 lat, -85.53 lon). The mine is located approximately 335 km east of Thunder Bay, ON., 35 km east of Marathon, ON. and currently consists of the operational Williams and decommissioned David Bell and Golden Giant complexes (closed in 2014 and 2006 respectively).

Lake Morphometry and Hydrology

Lim Lake

Lim Lake is an oval-shaped lake, 1 km long and 0.3 km wide with an average depth of 6 m and a maximum depth of 13 m. Lim Lake's bathymetry is bowl-like, sloping from the shores towards the deep zone in the approximate center of the lake (Figure 1.2, Appendix A). Lim Lake has a 1.3 X 10^6 m^3 volume, 0.301 km^2 (30.1 ha) surface area and an estimated 155-175 day residence time during discharge (Sigma Engineering 1984). From inflow to outflow, the lake is orientated along a north-west to south-east axis and is surrounded by a 0.4 km^2 watershed area, which provides brief inflow during spring melt and during heavy rain events (Sigma Engineering 1984). Outflow from the lake passes through a beaver dam and is consistent for most of the year, slowing during the winter months as the water elevation in the lake drops below the dam. There is unconsolidated flow that enters the lake off of the natural ridge on the northwestern shore that separates Lim Lake from the tailings management facility at the Hemlo Operation.

Frank Lake

Frank Lake is a U-shaped lake, 1.40 km long and 0.25 km wide with an average depth of 10 m and a maximum depth of 28 m. Frank Lake's bathymetry is more complex than Lim Lake's, having a main channel with two deep zones (12 m and 28 m deep) and two bays jutting North at either end of the main channel (8 m and 9 m deep) (Figure 1.3, Appendix A). Frank Lake has a 2.4 X 10^6 m^3 volume, 0.49

km^2 (49 ha) surface area and 270 day residency time (SENES Consultants Limited 1984). This residency time was calculated for the entire lake but the current meromictic state of the lake only has the top 6-11 m of the water column actively flowing through the lake, which likely shortens the residency time. From inflow to outflow the lake is orientated along a west to east axis and is surrounded by a 3.4 km^2 watershed (SENES Consultants Limited 1984), which provides inflow through an intermittent beaver dam for much of the year. Spring run-off promptly followed by discharge of effluent at a mutual location makes judging natural inflow difficult; however, an estimated 60% of flow into Frank Lake is from mine effluent (Weech and Orr 2009*b*). Outflow passes through a beaver dam and is consistent for most of the year, slowing during the winter months as the water elevation in the lake drops below the dam.

Historical Water Quality

Lim Lake

Some of the major studies performed on Lim Lake include; a Baseline Study in 1983 (Wood 1984), an Aquatic Environmental Assessment (AEA) in 1999 (Beak International Incorporated 2000*c*, International Incorporated 2000*d*) and Environmental Effects Monitoring (EEM) in 2005 (Orr and Stecko 2006*a*) and 2008 (Weech and Orr 2009*a*). Concentrations for relevant water quality parameters from these studies can be found in Table 1.1 (Appendix A). Parameters that have been the best indicators of effluent effects on Lim Lake include hardness, conductivity and sulphate. Baseline metal concentrations were all very low. The AEA in 1999 found that most parameters available for comparison with baseline data had increased (Beak International Incorporated 2000*c*). More specifically, concentrations of antimony, copper, molybdenum and nickel were elevated in the 1999 study compared to baseline (Beak International Incorporated 2000*c*). Antimony, copper, molybdenum and nickel had increased the most from baseline, although antimony and copper had decreased in Lim Lake in the years leading up to the study. The 1999 study found that mercury, arsenic, iron, lead and zinc had shown little change in Lim Lake since baseline data was collected (Beak International Incorporated

2000*c*). The 2005 EEM occurred just prior to the cessation of discharge in 2006 and all of the aforementioned water quality parameters remained elevated in Lim Lake but had decreased since the 1999 study (Orr and Stecko 2006*a*). Decreases in conductivity, hardness, major cations and most metals were found (Orr and Stecko 2006*a*). The second EEM study occurred 2 years after the cessation of discharge in 2008 and found that many water quality improvements had occurred since discharge cessation (Weech and Orr 2009*a*). All water quality parameters except iron had decreased. A major difference in water quality observed in the 2008 EEM compared to the 2006 EEM on Lim Lake was more elevated concentrations of nearly all parameters with increased depth (Weech and Orr 2009*a*). In general, all of the studies indicated that effluent effects became less apparent downstream of Lim Lake especially in Herrick Lake, which offered a great deal of dilution.

Frank Lake

Some of the major studies performed on Frank Lake include; Baseline Study in 1984 (SENES 1984), Aquatic Environmental Assessments in 1992 (ESP 1993), 1999 (Beak International Incorporated 2000*a*, Beak International Incorporated 2000*b*) and EEM's in 2005 (Orr and Stecko 2006*b*) and 2008 (Weech and Orr 2009*a*). Concentrations for relevant water quality data from these studies can be found in Table 1.2 (Appendix A).

Baseline water quality data showed low concentrations of all parameters (SENES 1984). The lake was slightly acidic, poorly buffered (low alkalinity) and had elevated aluminum, which is common for Canadian Shield lakes (SENES 1984). The AEA done in 1992 found that conductivity, hardness, alkalinity, calcium, magnesium, manganese, potassium, sodium, sulphate, nitrate, nitrite, antimony, barium, molybdenum, nickel, and strontium had increased compared to baseline data (ESP 1993). Increases in these major cations, anions and metals were sourced to mine effluent. Copper, iron and zinc concentrations had not been significantly altered. The 1999 AEA found that elevated parameters remained consistent with the 1992 study while others increased such as molybdenum and zinc (Beak International Incorporated 2000*c*). Both Cycle 1 and 2 EEM's found continued evidence of effluent effects on Frank Lake water quality (Orr and Stecko 2006*b* and Weech and Orr 2009*b*). Elevated levels of all of the aforementioned parameters from the 1992 study continued to remain elevated in Frank Lake in both studies. In both 2005 and 2008, samples taken in Frank Lake prior to initiation of spring effluent discharge demonstrated lower concentrations of many water quality parameters indicating dilution over winter and spring melt. In general, all studies found that effluent effects are most noticeable in Frank Lake and parameter elevations become nearly undetectable once Frank Creek meet the White River.

Spangle Lake (Reference Lake)

Although a number of lakes have been utilized for comparison of water quality in Lim and Frank Lake studies, Spangle Lake (49.62 lat, -85.88 lon) will be focused on here since it has been included in studies since the beginning of operations. It has been a common reference lake for both study lakes and it was sampled in the current study (Table 1.3, Appendix A). Spangle Lake is a J-shaped lake, 3.0 km long, 0.5 km wide (Harkness RA and Morgan JD) with a maximum depth of 16 m (Beak International Incorporated 2000*c*). The lake is orientated in a southwest-to-northeast direction with two deep zones of equivalent depth in the large bay and smaller bay to the northeast (Beak International Incorporated 2000*c*). Spangle Lake has not been influenced by mining activity and therefore has lower concentrations of nearly all metals and other ions in comparison to Lim and Frank Lakes. Consistently-elevated levels of aluminum and iron and occasionally-elevated levels of cadmium, chromium, cobalt, copper, iron and zinc compared to PWQO or Canadian Water Quality Guidelines (CWQG) have been measured in Spangle Lake which indicate that geological composition of the surrounding watershed has an influence on the lake's water quality (Harkness RA and Morgan JD, Beak International Incorporated 2000*a* and 2000*c*, Orr and Stecko 2006*a* and 2009*a*, Weech and Orr 2006*b* and 2009*b*). During summer months, Spangle Lake does show oxygen decreases in its lower strata, typically from 5-8 m to the bottom, depending on the sample year (ESP 1993, Beak International Incorporated 2000*a* and 2000*c*, Weech and Orr 2009*a* and 2009*b*). This lower-strata oxygen depletion in Spangle

Lake is solely due to summer thermal stratification since oxygen has always been replenished to bottom strata after fall turnover. Spangle Lake is dimictic since no chemical stratification exists within the lake as indicated by constant specific conductance through the water column (Beak International Incorporated 2000*b* and 2000*d*, Weech and Orr 2009*a* and 2009*b*).

Field Sampling Program

Water Sampling

Sampling for the project began in July 2011 and continued until fall 2013. Water sampling locations in both Lim and Frank Lakes are illustrated in Figures 1.2 and 1.3 respectively (Appendix A). Sample depth locations in Lim and Frank Lakes for the study duration can be viewed in Figures 1.4 and 1.5 respectively (Appendix A). Some additional multi-probe data was collected between these sample dates. Spangle Lake (reference lake) was sampled twice during the study in August 2011 and March 2012.

Sampling occurred at the deepest zones using a Wildco Teflon Kemmerer bottle as well as at the in/outlets when flow was observed. Sample bottles were rinsed once using sample water prior to filling. Field duplicates were performed once per sampling session and a traveling blank was performed once. Depth profiles for temperature, pH, specific conductance, salinity, DO, TDS, turbidity and chlorophyll *a* were obtained using a Hach Hydromet Hydrolab Datasonde 4a at 1 m intervals. Temperature, sp-cond and DO from the multi-probe were used to dictate depths of the epi-, meta- and hypolimnions as well as mixo- and monimolimnions and where samples were to be taken as stratification changed throughout the summer. The multi-probe was lowered to a particular depth and when readouts were stable, the data was recorded and the probe was lowered to the next depth. During summer months, an average of three samples were taken from the epi- and metalimnions and two samples from the hypolimnion. Three or more samples were taken from monimolimnion in Frank Lake. Fall, spring and winter sample depth locations were also dictated using the multi-probe. Chl *a* samples were taken at epi- and metalimnion sample depths in summer and select depths near the surface during fall, winter and spring. Inlets and outlets were also sampled for chl *a*. Chl *a* samples were sometimes taken from deeper waters however this was rare since most phytoplankton dynamics occur in strata near to the surface. Chl *a* samples were covered in tinfoil after sampling and frozen.

In the winter of 2013, multi-probe readings and water samples were collected from three additional locations in Frank Lake other than the deep zone (Figure 1.3, Appendix A). The two bays (both approx. 8 m deep) off of Frank Lake's main channel as well as the 12 m deep zone in the main channel were also sampled to determine if consistent water quality occurred horizontally and laterally across the entire lake in each stratum. Due to its smaller size and simpler bathymetry, Lim Lake was only sampled at its deep zone and no other locations within the lake system.

Characterization of the sulphur species in the lakes has been a main goal of the study because sulphur is the highest elevated constituent in both study lakes. The sulphur species of focus included total sulphur (TS), sulphate (SO_4^{2-}), thiosulphate ($S_2O_3^{2-}$) and hydrogen sulphide (H_2S).

H_2S Sampling

There was a potential for H_2S formation in the depths of Lim and Frank Lake based on the observed conditions (high sulphur concentrations and anoxic conditions). Obtainment of H_2S samples was performed utilizing a peristaltic pump attached to enclosed tubing and a needle. The tubing was lowered to a known depth congruent with the Kemmerer samples and the pump was used to draw the water up to the surface. The needle was used to inject water into sample bottles containing zinc acetate and sodium hydroxide preservatives. This set-up attempted to ensure that none of the H_2S that may be present in the sample was exposed to oxygen prior to preservation.

Laboratory Procedures

All laboratory analyses were conducted at the Lakehead University Environmental Laboratory (LUEL) which is ISO 17025 Accredited by Canadian Association for Laboratory Accreditation Incorporated (CALA).

Alkalinity and pH were measured using a Mettler DL53 Compact Titrator with Mettler Probe #DG111-SC calibrated at pH 4, 7 and 10. Conductivity was measured with a Mettler SevenMulti meter equipped with a conductivity module with automated temperature compensation calibrated at 200µS cm^{-1}. Fifty mL aliquots of unpreserved sample were used in the measurement of these parameters. Transport times, sample login and laboratory scheduling prevented a 24 hr measurement of these parameters however these parameters were measured within 48 hrs of sampling (Joncas 2012*c*, Joncas 2012*a*). Hardness was calculated using the formula (American Water Works Association *et al* 2006):

$$\textbf{Hardness (mg L}^{-1}\textbf{) = (2.497*Calcium (mg L}^{-1}\textbf{)) + (4.118*Magnesium (mg L}^{-1}\textbf{))}$$

Total dissolved and suspended solids (TDS and TSS) were measured within 7 days of sampling. Gravimetric analysis was employed using a 200 mL unpreserved sample aliquot and filtering it through a pre-weighed 0.45 µm glass filter using vacuum filtration. The filter was kept for TSS analysis and 50 mL of the filtered sample was placed in a pre-weighed beaker and used for TDS analysis. Both the filters and the filtered 50 mL aliquots were heated in ovens for 12 hrs at 103°C and 180°C respectively. Final weighing occurred using an OHAUS Analytical Scale calibrated to 5 decimal places and reported values were presented as the weight per volume of the entire sample (Joncas 2012*b*).

Total metal samples were preserved the day of sampling using 3-5 drops of 50% nitric acid (HNO_3) and analysis was performed using a 50 mL sample aliquot with 0.4 mL of concentrated HNO_3 added. Samples were heated at 95°C in a CEM Mars 5 microwave unit until a five-fold concentration of the sample had been achieved (~24 hrs). Sample volumes were then increased up to 10 mL with double distilled water (DDW) and mixed by inversion. Total and dissolved metals were analyzed using a VarianPro Inductively Coupled Argon Plasma Spectrometer (ICP-AES) for Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Si, St, V, and Zn (Joncas 2012*d*). If a particular metal was continually below the detection limit, it was not deemed critical for further analysis and after a number of sampling sessions, Be, Cd, Cr, Pb and Vd were removed from Lim and Frank Lake analysis as well as Co from the

Lim Lake analysis (Joncas 2012*e*).

Anions including chloride (Cl^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrate (NO_3^-) and nitrite (NO_2^-) were analyzed using 5 mL aliquots of unpreserved sample. A 5-25-fold dilution of many of the Frank Lake samples occurred due to the high concentration of many of the anions. A Dionex ICS-1100 Ion Chromatograph (IC) with an AS14 separation column in conjunction with an AS-DV automated sampler was used to analyze the samples.

Total phosphorus (TP) was analyzed using a SKALAR Sans+ automated chemistry analyzer (50 mm flow cell, 880 nm filter) with Flowaccess software. Ten to thirty mL of unpreserved sample was mixed with potassium peroxodisulfate and a disodium tetraborate solution and UV radiation was used to destroy organic phosphates. Sulfuric acid was added to digest ortho-phosphates at 97°C. Neutralization occurred via sodium hydroxide. A phosphor-molybdic acid complex was formed by reacting ammonium heptamolybdate and potassium antimony (III) oxide tartrate in acidic media with diluted phosphate solutions. The phosphor-molybdic acid complex was reduced by ascorbic acid and its blue colour could be spectrophotometrically measured at 880 nm (Joncas and Walford 2012*a*).

Total nitrogen (TN) was analyzed using the SKALAR Sans+ automated chemistry analyzer with SA1070 (30 mm flow cell, 8mL sample cups) and version 6.2 software. Ten to thirty mL of unpreserved sample was mixed with potassium peroxodisulfate/sodium hydroxide solution and then borax buffer after being heated to 90°C. This solution was then UV digested to convert all nitrogen forms into nitrate which can converted to nitrite using a cadmium copper redactor which can be measured using the Greiss reaction at 540 m. Total Kjeldahl Nitrogen was calculated by subtracting NO_2^- and NO_3^- values from TN values (Joncas and Walford 2012*b*).

Ammonia nitrogen (N-NH_3) was analyzed using a Dionex ICS-1100 Ion Chromatograph with sample aliquots obtained from the routine bottle. Approximately 5 mL aliquots were mixed with a stream of methanesulfonic acid eluent and passed through the column at high pressure. Various cations were separated based on attraction to the column and conductivity of the peaks were then measured with a conductivity cell. A Dionex IC-120 (4 mm system) with an ionpac CS16 analytical column (5x250 mm) and an ionpac CG16 guard column (5x50 mm) in a weakly acidic medium, an AS40 autosampler and PEAKNET version 4.30 version software were used to analyze the samples (Raitsakas and Walford 2011).

Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were measured with the SKALAR Sans+ automated chemistry analyzer. Sample aliquots were acidified upon introduction to the SKALAR and flushed with nitrogen gas to remove the inorganic carbon. The sample was then oxidized with UV radiation in acid-persulfate to convert carbon to CO_2. Dialysis was performed and then CO_2 was measured by determining change in absorbance of a weakly buffered alkaline solution with a phenolphthalein indicator.

Sulphide analysis to measure H_2S occurred using a primary/peer-reviewed method (Cline 1969). A Cary 5e spectrophotometer was used for the spectrophotometric analysis.

When developing total sulphur to sulphate ratios, all of the sulphate concentrations were multiplied by 0.33 in order to obtain only the mass of sulphur from each mg L^{-1} sulphate concentration and exclude the mass of the oxygen molecules.

Chl *a* sample analysis involved thawing and filtering 1 L of sample through a ≥5 μm filter using vacuum filtration and then dissolving the filter and its contents in 15 mL of 90% acetone using periodic vortexing and then settling for 18-24 hrs. Spectrophotometric analysis using the Cary 5e spec at 660, 670, 680 and 750 nm was used to give ug L^{-1} of chl *a*.

Isopleth Development

Isopleths (contours of depth, time and parameter concentrations) were used to display the data because they allowed for a large amount of data to be displayed in a single figure. Although line graph interpretation can be simpler, comparing line graphs from many data sets can be cumbersome. To develop the isopleths, Golden Software's SURFER 12 was used. A grid file was developed for each parameter to produce a contour map of depth (y-axis), time (x-axis) and concentration (z-axis).

Triangulation with linear interpolation was used as the gridding method to develop the contour plots because it resulted in the best representation of the data whereas other gridding methods such as kriging or nearest neighbor resulted in contour plots that were largely different from observed data.

Statistical Analysis

SPSS-Statistical Software (Ver. 23) was used to perform hierarchical cluster analyses for water quality data from Lim and Frank Lakes for 2011 and 2013. The data was log-transformed in Excel prior to statistical calculations due to the fact that the parameters were measured with differing scales (units: mg L^{-1}, ug L^{-1}, pH, °C). The data was also standardized to have a standard deviation of 1. Both transformation and standardization are common practices when statistically analyzing water quality data (Baxter 1995, Cao *et* al 1999). An average-linkage (between groups) clustering technique was utilized. "Chaining" was minimal using this method and non-monotonic inversions were absent. Detection limit (DL)*0.5 was used for all <DL results however parameters that had <DL results for a majority of the samples were not included in the cluster analysis. Pearson correlation was used as the proximity index (measure of dissimilarity).

A univariate ANOVA was also performed to determine variation significance by layer (1=epilimnion or mixolimnion, 2=metalimnion or chemocline and 3=hypolimnion or monimolimnion), year (1=2011, 2=2012 or 3=2013) and season (Spring=ice-off, Summer=thermal stratification, Fall=thermal stratification deteriorating, Winter= thermal stratification absent/ice-on). A significance level of $p<0.05$ was used. November data was considered winter data because ice formation occurred the day before or after sampling during this month in all years. Percent change in the average concentration of each parameter from 2011 to 2013 included data from all of 2011 For Lim Lake, when calculating percent change in water quality parameters in 2011 versus 2013; data from the whole water column was used. For Frank Lake, when calculating this percent change, an individual percentage was calculated for each layer (mixo-, chemo- and monimolimnion) because these layers were present throughout the study. Calculating three separate percentages made it possible to discern which layers had the most or least change.

Results

Statistical Analyses – Water Chemistry

The cluster analyses and ANOVAs for both study lakes identified parameters that fluctuated similarly through the water column and varied significantly between layers, years and seasons for all data. If certain parameters increased and/or decreased similarly through the water column at similar times during the study, they would be grouped together and form clusters. Ultimately this helped to illustrate parameters that responded similarly to specific events in the field such as natural remediation and turnover (Lim Lake), prolonged meromixis and fluctuations in effluent discharge (Frank Lake) or the May 2013 rain event (both lakes). The clusters resulting from the 2011 Lim (Figure 1.6) and Frank Lake (Figure 1.8) data had a higher level of dissimilarity (had longer internodes) than the 2013 data clusters for these lakes (Figure 1.7 and Figure 1.9 respectively). Similar parameters tended to cluster together and some similarities between clusters were observed from 2011 versus 2013. It is important to note that some of the parameters (silicon, total phosphorus, nitrate, ammonia, total kjeldahl nitrogen, dissolved organic and inorganic carbon) were not measured after June 2013 and so less data was available for analysis and likely had a small impact on the cluster results for both lakes.

Tables 1.4 and 1.5 illustrated the parameter averages in each layer in Lim and Frank Lakes respectively in 2011 and 2013, the percent change between these years as well as variance significance. Tables 1.6 to 1.8 in Appendix B demonstrate the actual significance results for layers, years and seasons in Lim Lake respectively. The same results are demonstrated for Frank Lake in Tables 1.9 to 1.11 respectively in Appendix B.

Lim Lake

In 2011, the parameters in Cluster 1: (Ca, hardness, Na, K, Sr, Ba, Mg, alkalinity, Fe, Mn, sp-cond, TDS and Ni) (Figure 1.6) had much higher concentrations in lower strata, especially in summer 2011, but equalized during fall 2011 turnover. These parameters largely comprised the TDS of the lake. Ni's presence in the cluster was debatable and it could have been considered an independent parameter. Cluster 2's parameters (DIC, Cl, sulphate and total sulphur) also demonstrated large concentration increase with depth but also showed an increase in surface strata during fall 2011, which made it dissimilar from cluster 1. Cluster 3's parameters (ammonia, TotP and Si) all increased with depth during summer but decreased greatly in concentration during fall compared to other parameters. The parameters of both Clusters 4 (temp and pH) and Cluster 5 (DO, NO_3 and Cu) had a greater magnitude in upper strata and decreased with depth; however, the gradient of decrease was not quite as smooth for Cluster 5. TKN, Zn, DOC, chl *a* and Al were all independently-varying parameters in 2011. TKN increased with depth like cluster 1 and 2 but showed very little surface strata variability in fall, which made it unique. Chl *a*, Al and Zn demonstrated sporadic increases in isolated strata but these increases differed slightly both spatially and temporally. DOC had a relatively constant concentration from surface to bottom in 2011.

In 2013, similar clusters resulted (Figure 1.7); however some parameters joined a different cluster compared to 2011. Cluster 1 was maintained and contained (Ca, hardness, total sulphur, K, Na, Sr, Mg, sp-cond, sulphate, Cl, Zn, TDS, Ni, Ba, Fe, alkalinity, Mn, TKN and DIC). Cluster 1 gained all of the parameters of Cluster 2 in 2011 (total sulphur, sulphate, Cl and DIC) as well as Zn and TKN, which clustered independently in 2011. The common trend with the Cluster 1 parameters was an increasing concentration with depth early in the year, surface decrease during the rain event and continued decrease and eventual equalization throughout the water column after fall turnover. The magnitude of increase with depth varied for each parameter. The parameters of Cluster 2 (Chl *a* and pH) demonstrated higher levels in surface strata but remained largely unaltered during the rain event. Cluster 3 parameters (temp, Al and Tot P) also demonstrated higher levels near the surface but demonstrated an isolated surface increase during the rain event of May 2013. Cluster 4 (DO, NO_3 and Cu) was the exact same as Cluster 5 in 2011. Higher concentrations of these parameters were found in surface strata.

Ammonia, Si and DOC were all independent parameters in 2013. These parameters were all only measured up to June 2013. Ammonia and Si increased very slightly with depth but both responded differently to the rain event. Ammonia almost completely eliminated from the water column after the rain event whereas Si increased slightly in all strata during the rain event. DOC was largely constant from surface to bottom but increased greatly in surface water after the rain event.

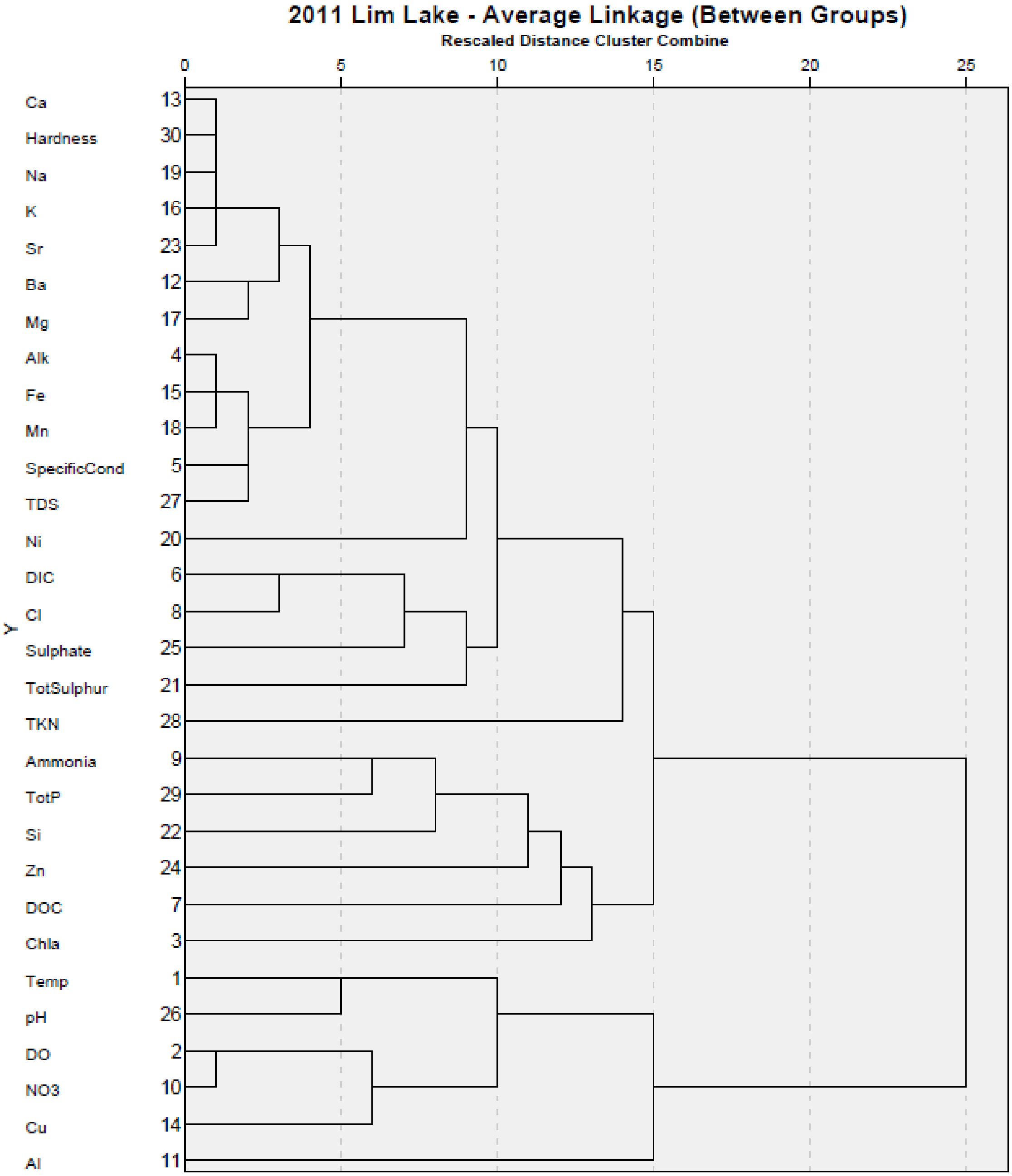


Figure 1.6. Hierarchical cluster analysis of Lim Lake water quality parameters for Jul 2011-Nov 2011 using the average-linkage (between groups) cluster method.

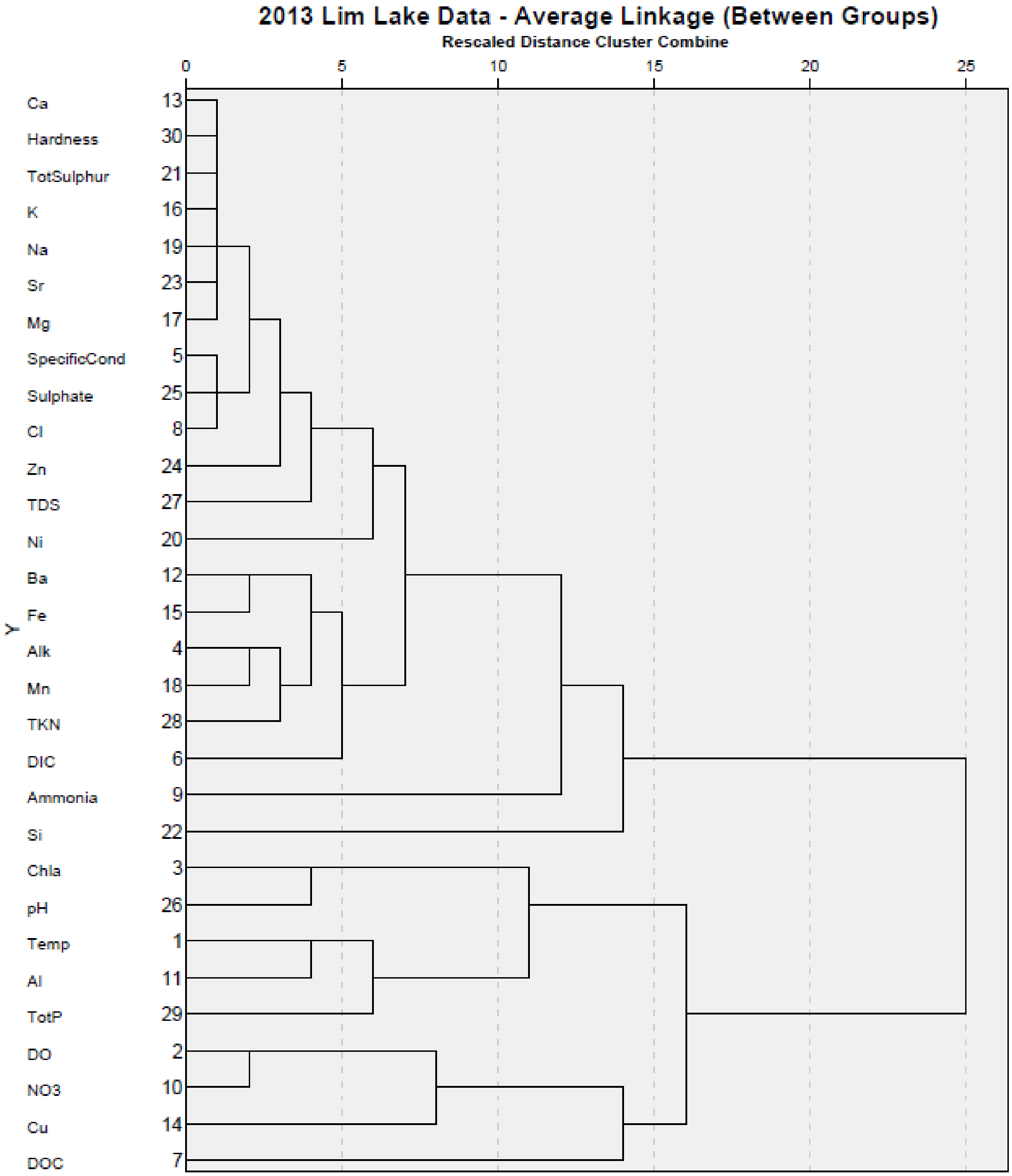


Figure 1.7. Hierarchical cluster analysis of Lim Lake water quality parameters for Feb 2013-Nov 2013 using the average-linkage (between groups) cluster method.

The ANOVAs indicated that a majority of parameters varied significantly between layers (epi-, meta- and hypolimnion). These parameters included temperature, DO, alkalinity, sp-cond, DIC, ammonia, nitrate, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Si, Sr, pH, TDS and hardness. Although many of these parameters clustered differently from each other, they all were part of clusters that varied with some magnitude through the water column, whether it was increasing or decreasing with depth. Parameters not demonstrating a significant variance with depth included chl *a*, DOC, Cl, Al, total sulphur, sulphate, Zn, TKN and TotP. In 2011, all of these parameters except total sulphur, sulphate and TotP clustered individually due to varying uniquely in the water column. Although total sulphur, sulphate and TotP increased markedly with depth in summer 2011, after the fall 2011 turnover, their increase in concentration with depth during other stratification periods was much less for the remainder of the study.

All parameters excluding DO, Al, Ba, Fe, Mn, Zn and TotP varied significantly between years. As indicated in Table 1.4, all of these parameters, except Mn (sig. level=0.054), increased or decreased by 0-21% on average from 2011 to 2013. All other parameters demonstrated an increase or decrease of >21% magnitude on average from 2011 to 2013; excluding pH, alkalinity, DOC, Mg and Ni.

The only parameters that did not demonstrate significant variability with season were DO, DOC, Al and Ni. The significance level for DO (0.065) was a much lower magnitude than the other parameters and was close to the significance level of $p<0.05$. DOC demonstrated independent variability since it was not part of a cluster in either 2011 or 2013 and the same occurred for Al in 2011.

To summarize, significant variation in many parameters were observed between layers, years and seasons in Lim Lake. A variety of these parameters varied in unison and formed distinctive clusters. The recovering state of Lim Lake and occurrence of a full water column turnover monomictic mixing regime in the lake as well as the rain event of 2013 are the main influences on the concentration variations observed.

Table 1.4. Average parameter concentrations in Lim Lake layers and whole-lake percent change from 2011/2013. Associated ANOVA significance results for layers, years and seasons also displayed.

Parameter	**Epi**		**Meta**		**Hypo**		**Whole Year Average**		**Whole Year % Change 2011-2013**
	2011	**2013**	**2011**	**2013**	**2011**	**2013**	**2011**	**2013**	
Temp ^{a,b,c,d}	15.77±7.58	6.48±5.32	11.10±4.67	4.58±3.74	5.47±0.89	3.78±0.48	10.00±6.77	4.33±3.51	-56.71
DO ^{b}	9.33±1.08	9.69±0.79	5.84±4.72	8.82±2.20	1.27±4.83	3.82±3.12	6.96±4.49	7.30±3.30	4.91
Chl a ^{a,c,d}	1.32±0.44	3.04±1.17	2.23±0.99	1.99±1.52	1.48±0.24	2.03±1.30	1.50±0.57	2.72±1.28	80.90
pH ^{a,b,c,d}	7.08±0.18	7.13±0.07	6.81±0.13	7.05±0.17	6.76±0.09	6.81±0.14	6.92±0.19	7.00±0.17	1.23
Alkalinity ^{b,c,d}	34.69±4.42	31.56±3.90	41.58±10.83	34.08±3.37	58.89±10.96	39.88±4.40	43.45±12.2	35.30±4.91	-18.74
Hardness ^{b,c,d}	200.06±19.40	153.80±27.58	237.68±30.10	172.46±26.51	277.59±29.04	187.82±24.15	231.04±37.60	166.53±27.3	-27.92
Sp-Cond ^{a,b,c,d}	649.73±55.99	451.86±85.27	750.50±127.97	510.56±78.42	886.18±95.81	562.17±69.10	113.10±121.0	59.41±82.32	-47.47
Tot Sulphur ^{c,d}	109.84±45.55	54.29±12.31	96.29±15.10	62.38±11.35	143.29±54.88	67.98±10.03	306.66±46.49	221.47±11.61	-27.78
Sulphate ^{c,d}	265.53±95.95	202.51±58.88	316.24±138.51	235.18±59.13	329.10±129.15	269.63±60.67	736.36±117.89	496.97±61.89	-32.51
TDS ^{b,c,d}	421.60±33.23	300.83±57.94	483.40±74.03	339.22±57.83	593.96±63.76	364.30±57.53	484.70±82.08	324.95±58.94	-32.96
DIC ^{b,c,d}	7.41±1.41	5.09±2.08	10.14±3.84	5.91±1.77	12.18±3.14	7.67±1.12	9.51±3.18	6.46±1.92	-32.08
DOC ^{c}	8.25±0.77	10.14±1.19	8.57±0.69	9.68±0.88	9.14±0.58	9.73±0.53	8.55±0.75	9.82±0.87	14.81
Cl ^{c,d}	14.37±3.33	9.88±1.53	17.87±6.34	10.99±1.33	19.45±5.54	12.62±1.84	16.75±5.10	10.91±1.84	-34.85
Ammonia ^{b,c,d}	0.36±0.18	0.15±0.03	0.90±0.58	0.18±0.09	2.42±0.94	0.41±0.32	1.04±0.96	0.27±0.24	-73.70
NO_3 ^{b,c,d}	0.14±0.02	0.19±0.02	0.11±0.07	0.19±0.02	0.03±0.05	0.16±0.07	0.11±0.06	0.18±0.05	67.03
TKN ^{c,d}	0.90±0.68	0.40±0.12	2.20±1.20	0.42±0.14	2.72±1.92	0.71±0.33	1.56±1.46	0.54±0.27	-65.26
TotP ^{d}	0.0081±0.006	0.0129±0.008	0.0138±0.012	0.0114±0.005	0.0286±0.029	0.0109±0.003	0.0146±0.02	0.0116±0.005	-20.55
Al ^{b}	0.057±0.078	0.061±0.17	0.032±0.008	0.046±0.007	0.037±0.018	0.041±0.010	0.044±0.052	0.047±0.013	5.72
Ba ^{b,d}	0.022±0.002	0.022±0.001	0.025±0.004	0.021±0.001	0.026±0.002	0.026±0.004	0.024±0.003	0.023±0.003	-4.33
Ca ^{b,c,d}	75.47±7.35	57.61±10.53	90.02±11.51	64.73±10.19	105.66±11.34	70.73±9.34	87.50±14.57	62.49±10.50	-28.59
Fe ^{b,d}	0.052±0.032	0.058±0.042	0.318±0.357	0.067±0.039	0.062±0.298	0.426±0.365	0.262±0.30	0.211±0.28	-19.41
K ^{b,c,d}	12.16±1.28	8.64±1.80	14.85±2.48	9.76±1.66	17.44±2.02	10.91±1.61	14.27±2.63	9.47±1.80	-33.62
Mg ^{b,c,d}	2.82±0.255	2.42±0.318	3.13±0.339	2.63±0.265	3.34±0.215	2.72±0.214	3.05±0.31	2.55±0.27	-16.30
Mn ^{b,d}	0.062±0.04	0.047±0.02	0.331±0.31	0.072±0.02	0.584±0.22	0.264±0.13	0.264±0.26	0.138±0.12	-47.49
Na ^{b,c,d}	34.28±3.50	25.34±5.69	42.06±6.47	28.64±5.37	49.02±5.16	31.69±5.28	40.33±7.14	27.36±5.66	-32.15
Ni ^{b,c}	0.014±0.001	0.012±0.001	0.017±0.001	0.014±0.001	0.015±0.002	0.015±0.001	0.015±0.002	0.014±0.001	-9.18
Si ^{b,c,d}	0.39±0.24	0.69±0.12	0.64±0.29	0.72±0.13	1.08±0.44	0.99±0.18	0.58±0.40	0.83±0.20	42.34
Sr ^{b,c,d}	0.070±0.008	0.057±0.009	0.070±0.03	0.062±0.008	0.102±0.013	0.068±0.007	0.081±0.02	0.061±0.006	-24.08
Zn ^{d}	0.006±0.0038	0.005±0.0041	0.014±0.010	0.007±0.0037	0.010±0.0061	0.006±0.0029	0.008±0.008	0.006±0.003	-20.46

[a] All units are in mg L^{-1} except Sp-Cond (µS cm^{-1}), Chl *a* (µg L^{-1}) and pH (units).
[b] Significant difference ($p < 0.05$) between depths.
[c] Significant difference ($p < 0.05$) between years.
[d] Significant difference ($p < 0.05$) between seasons.

Frank Lake

In 2011, the most definitive cluster with the most parameters was Cluster 1 (Ca, hardness, TDS, Mo, sp-cond, Mn, Ni, alkalinity, Al, Ba, sulphate, K, Na and DIC) (Figure 1.8). All of these parameters demonstrated lower concentrations in the mixolimnion versus the monimolimnion but also showed an increased mixolimnion concentration during fall 2011. Parameters of Cluster 2 (chl *a*, Si and DOC) formed a loose cluster but all of these parameters demonstrated a relatively constant concentration from surface to bottom and demonstrated a whole water column decrease towards fall. Parameters of Cluster 3 (DO, Sr, temp and pH) were all lower in magnitude below the chemocline. Parameters of Cluster 4 (NO_3, Cl, ammonia and Mg) all demonstrated little to no increase in concentration with depth but during fall, their surface strata concentration increased markedly. Total sulphur, Zn, TKN, TotP and Fe all varied independent within the water column. Total sulphur increased to a lesser magnitude with depth but showed a substantial increase in fall 2011. TKN and Fe varied little in the water column but TKN showed successive whole-water column decrease into fall. Zn and TotP both showed increases at isolated depths but differed spatially and temporally from each other.

In 2013, Cluster 1 (Ca, hardness, TDS, sp-cond, sulphate, total sulphur, K, Na, Mg, NO_3, Cl, Ba, Sr, Alk, Mo, DIC and TKN) was similar to Cluster 1 in 2011 (Figure 1.9). Total sulphur, Mg, NO_3, Cl, Sr and TKN joined Cluster 1 and Mn, Ni and Al were removed from it. This cluster was formed by parameters that again, increased in concentration below the chemocline and demonstrated a particular decrease in surface concentration after the May 2013 rain event. The residual effect of these decreased surface concentrations occurred for the remainder of the year. Cluster 2 (ammonia and pH) had a relatively higher level of dissimilarity but both showed higher concentrations in the mixolimnion aside from isolated strata where ammonia concentrations were particularly high. Cluster 3 (Si, Zn, Mn, Ni and TotP) also had a relatively high level of dissimilarity but concentrations increased slightly with depth, decreased in upper strata after the rain event but increased again in these upper strata towards the fall. Cluster 4's parameters (chl *a*, DOC, Al, DO and Fe) were more elevated above the mixolimnion in connection with the rain event. Only temperature varied independently in 2013.

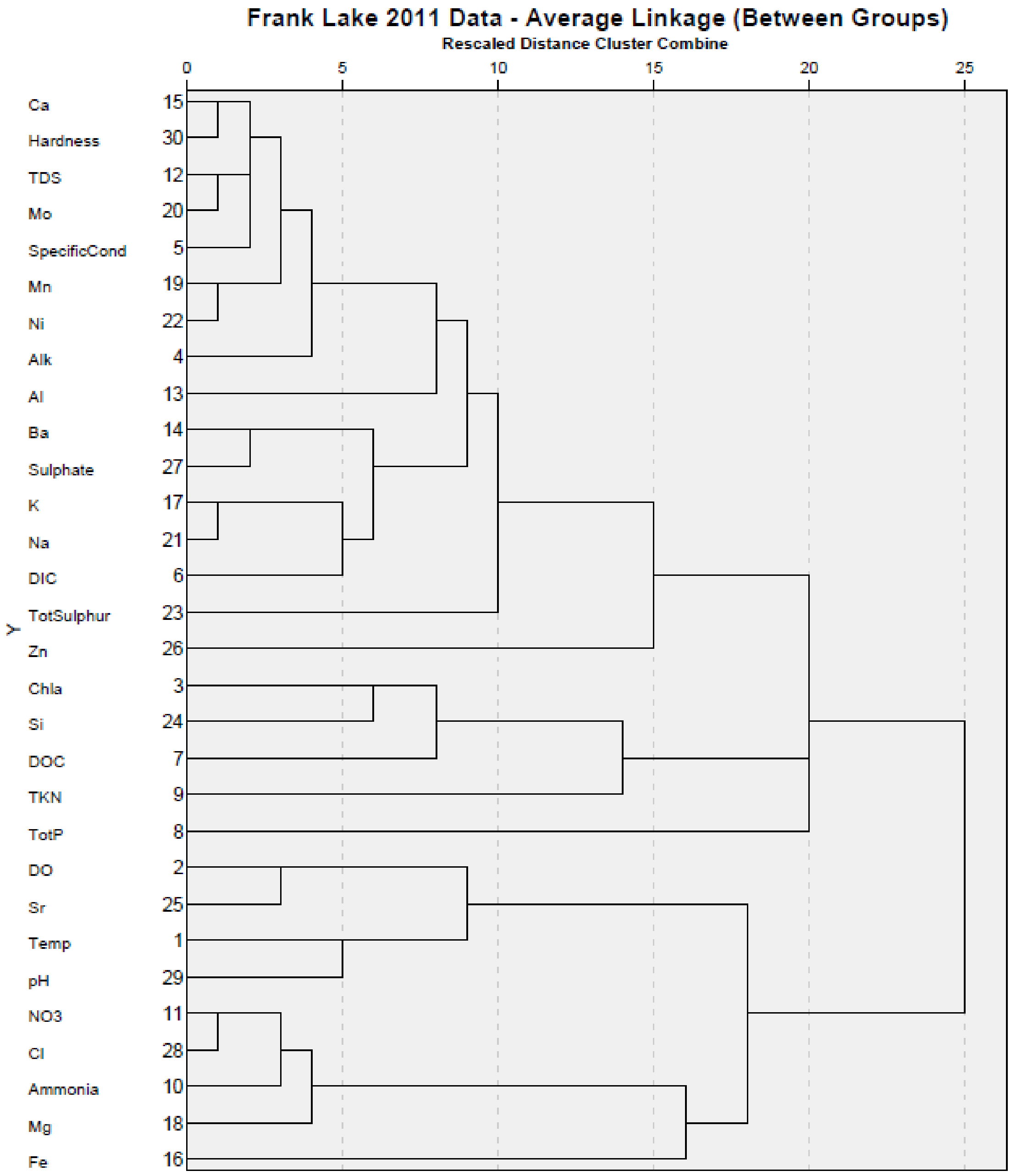


Figure 1.8. Hierarchical cluster analysis of Frank Lake water quality parameters for Jul 2011-Nov 2011 using the average-linkage (between groups) cluster method.

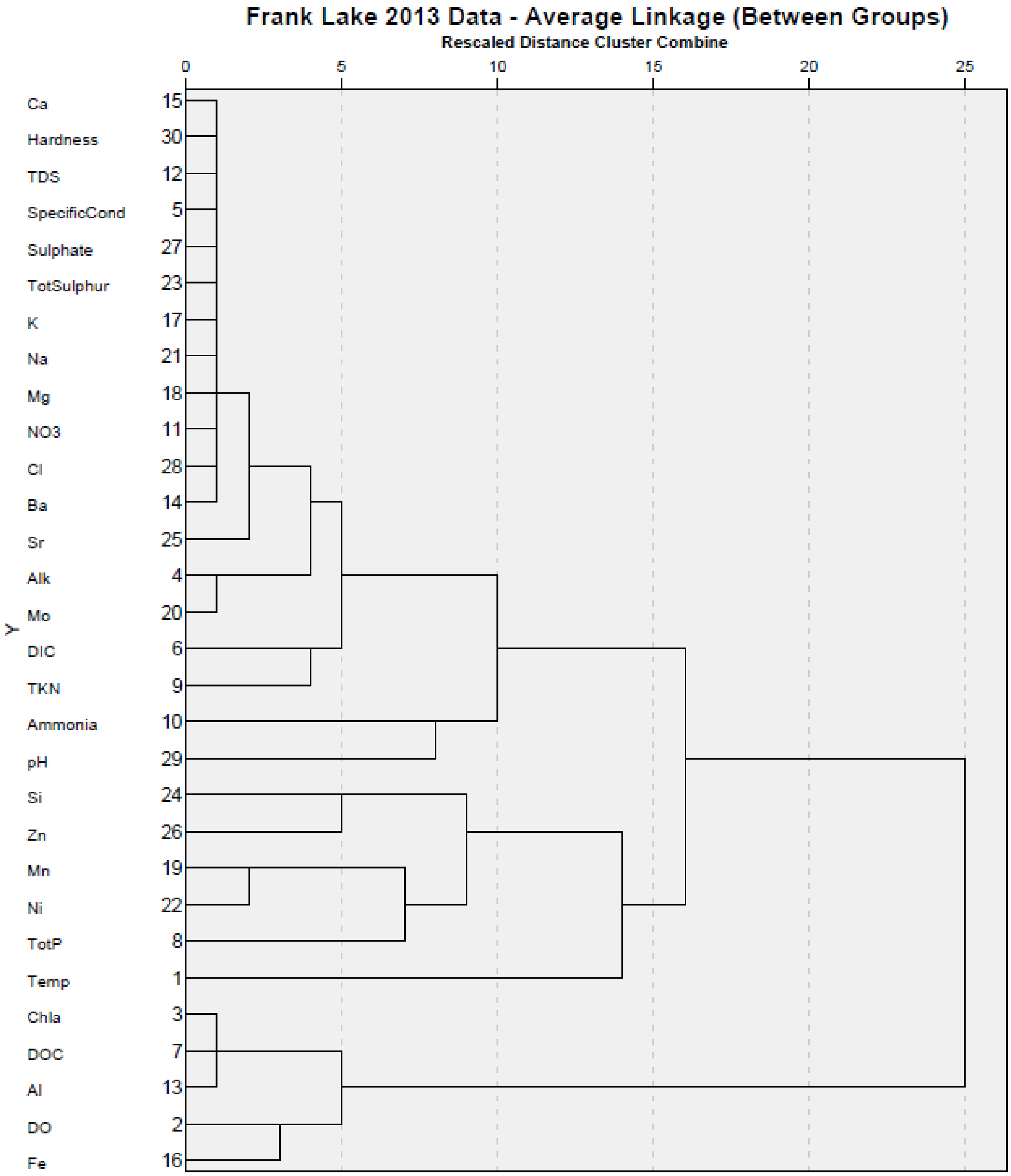


Figure 1.9. Hierarchical cluster analysis of Frank Lake water quality parameters for Feb 2013-Nov 2013 using the average-linkage (between groups) cluster method.

The ANOVAs indicated that a majority of parameters varied significantly between layers (mixo-, chemo- and monimolimnion). These parameters included temperature, DO, alkalinity, sp-cond, DIC, TotP, TKN, ammonia, NO_3, TDS, Al, Ba, Ca, Fe, K, Mn, Mo, Na, Ni, total sulphur, Si, Sr, Zn, sulphate, pH and hardness. In 2011, all of these parameters except Fe and TKN either belonged to clusters that varied in some capacity with depth or showed an independent trend of depth variability and formed an independent cluster. In 2013, Fe and TKN were influenced by the May rain event resulting in them merging with clusters that demonstrated layer variability in 2013. Parameters that did not vary significantly with depth were chl *a*, DOC, Mg and Cl. Chl *a* and DOC were part of the same cluster (Cluster 2) in 2011, as were Mg and Cl (Cluster 4). In general, these parameters did not vary greatly with depth aside from alterations in fall 2011, March 2012 and May 2013 and the clusters they were part of in 2011 and 2013 were representative of their concentration changes at these times.

The number of parameters that varied significantly from 2011 to 2013 and the number that did not were the same, dividing the parameter list in half. Table 1.5 specified the percent change of each parameter in 2011 versus 2013 in the mixo-, chemo- and monimolimnions of each year. Parameters that did demonstrate variability between the years included temperature, chl *a*, sp-cond, TKN, ammonia, $NO_{3,}$ TDS, Al, Ba, K, Mg, Mo, total sulphur, Si and Cl. In general, most of the parameters that demonstrated a significant difference in years demonstrated either a decrease or increase in all three layers (i.e. all three layers had either a positive or negative % change) (Table 1.5). Al, Ba, Cl and Si were some exceptions to this. Parameters that did not demonstrate significant variability over the years were DO, alkalinity, DIC, DOC, TotP, Ca, Fe, Mn, Na, Ni, Sr, Zn, sulphate, pH and hardness. Most of these parameters demonstrated increase in some layers but decreases in others when comparing 2011 and 2013 (Table 1.5).

Regarding seasons, all parameters except DO, alkalinity, DOC, TDS, Al, Fe, Mn, Na, Ni, Sr and pH showed significant variability. A majority of these parameters also demonstrated variability between years as discussed above.

To summarize, significant parameter concentration variations between layers, years and seasons occurred in Frank Lake and clustered groups of parameters varied in unison. Undoubtedly, the meromictic stability and incomplete turnover that occurs in Frank Lake is a main influence on water quality in the lake.

In addition, the alterations of effluent discharge into the lake through the year and the rain event of 2013 largely impacted the concentration variations observed during the study.

Table 1.5. Average parameter concentrations in Frank Lake layers during 2011/2013 and associated ANOVA significance results for layers, years and seasons. Significant difference between years highlighted in gray.

Parameter	Mixolimnion		Chemolimnion		Monimolimnion		% Change 2011 vs. 2013		
	2011	**2013**	**2011**	**2013**	**2011**	**2013**	**Mixo**	**Chemo**	**Monimo**
Temp [a,b,c,d]	12.47±6.96	4.46±5.10	6.35±2.82	3.96±0.34	4.84±0.02	4.48±0.11	-64.26	-37.57	-7.31
DO [b]	9.77±1.08	9.13±1.88	4.28±3.11	5.64±2.81	0.14±0.22	0.36±0.33	-6.56	31.91	162.18
Chl a [a,c,d]	0.52±0.14	2.11±0.58	1.03±0.16	1.58±0.50	0.83±0.09	1.33±0.09	307.13	54.00	60.60
Alkalinity [b]	34.54±2.27	28.07±7.55	33.76±1.94	30.37±1.76	43.59±1.04	46.05±4.79	-18.71	-10.03	5.64
Sp-Cond [a,b,c,d]	1988.00± 207.59	1531.60± 435.24	2050.44± 123.14	1911.35± 145.69	2314.55± 56.63	2211.58± 78.69	-22.96	-6.78	-4.45
DIC [b,d]	6.35±3.02	7.98±3.55	6.34±2.31	6.07±1.67	11.37±1.35	7.59±2.41	25.81	-4.28	-33.27
DOC	4.51±0.63	7.90±2.68	5.67±0.80	5.41±1.04	5.12±0.22	4.56±1.07	75.00	-4.49	-10.86
TotP [b,d]	0.009±0.01	0.011±0.00	0.013±0.01	0.007±0.01	0.012±0.01	0.018±0.01	30.13	-45.62	45.77
TKN [b,c,d]	9.69±10.88	13.03±6.82	12.39±11.44	18.34±2.52	8.70±4.35	14.74±2.55	34.45	48.05	69.49
Ammonia [b,c,d]	4.34±1.53	1.70±1.21	3.17±1.40	1.91±1.21	2.93±0.74	0.40±0.95	-60.75	-39.78	-86.53
NO_3 [b,c,d]	30.53±10.97	18.27±7.26	24.08±8.75	22.96±3.90	22.85±4.86	17.86±3.22	-40.14	-4.69	-21.80
TDS [b,c,d]	1407.81± 134.32	1086.53± 324.76	1513.29± 62.05	1367.36± 117.41	1761.95± 33.03	1661.15± 64.39	-22.82	-9.64	-5.72
Al [b,c]	0.035±0.01	0.113±0.07	0.048±0.01	0.052±0.01	0.055±0.01	0.041±0.01	225.23	7.60	-24.87
Ba [b,c,d]	0.020± 0.003	0.017± 0.003	0.018± 0.002	0.019± 0.001	0.024± 0.001	0.022± 0.001	-13.38	7.89	-8.87
Ca [b,d]	176.53± 21.53	134.09± 38.95	195.06± 23.69	171.15± 18.74	255.12± 17.52	236.24± 21.46	-24.04	-12.26	-7.40
Fe [b]	0.018± 0.004	0.080± 0.067	0.024± 0.004	0.026± 0.010	0.019± 0.012	0.009± 0.010	343.33	9.86	-55.28
K [b,c,d]	75.05±9.25	59.23±17.80	75.53±5.31	73.10±6.01	76.95±2.56	75.17±3.80	-21.08	-3.21	-2.31
Mg [c,d]	4.46±0.42	3.53±0.90	4.38±0.22	3.96±0.36	4.18±0.39	4.08±0.18	-20.82	-9.59	-2.34
Mn [b]	0.037±0.02	0.062±0.01	0.123±0.07	0.090±0.04	0.458±0.03	0.384±0.09	68.77	-27.01	-16.07
Mo [b,c,d]	0.203±0.03	0.146±0.04	0.240±0.02	0.181±0.03	0.299±0.01	0.258±0.02	-28.03	-24.65	-13.46
Na [b]	161.12± 19.08	145.32± 45.57	164.13± 10.68	177.52± 24.33	173.38± 6.29	186.34± 19.26	-9.80	8.16	7.47
Ni [b]	0.023± 0.003	0.024± 0.006	0.038± 0.008	0.029± 0.005	0.073± 0.003	0.055± 0.009	4.45	-24.87	-23.91
Tot Sulphur [b,c,d]	336.25± 148.05	205.27± 64.63	365.06± 162.95	262.35± 26.93	439.78± 161.68	333.91± 21.69	-38.95	-28.14	-24.07
Si [b,c,d]	0.50±0.30	0.91±0.18	1.07±0.35	0.90±0.15	1.03±0.38	1.35±0.29	84.07	-15.53	30.16
Sr [b]	1.84±0.23	1.51±0.42	1.63±0.22	1.78±0.11	0.84±0.09	1.13±0.21	-18.29	9.31	35.13
Zn [b,d]	0.007± 0.005	0.007± 0.003	0.008± 0.004	0.007± 0.003	0.014± 0.007	0.010± 0.004	13.85	-8.75	-25.94
Sulphate [b,d]	1078.73± 398.94	700.96± 285.50	894.99± 383.07	935.11± 165.67	1523.16± 340.08	1256.06± 157.89	-35.02	4.48	-17.54
Cl [c,d]	68.29± 25.80	43.56± 15.83	52.79± 19.51	56.12± 7.26	57.99± 11.97	50.05± 6.54	-36.21	6.31	-13.68
pH [a,b]	7.09±0.145	7.01±0.141	6.63±0.140	6.88±0.142	6.54±0.044	6.72±0.048	-1.09	3.77	2.81
Hardness [b,d]	459.15± 55.16	349.34± 100.85	505.09± 59.53	443.65± 48.13	654.26± 43.75	606.70± 53.85	-23.91	-12.16	-7.27

[a] All units are in mg L^{-1} except Sp-Cond (µS cm^{-1}), Chl *a* (µg L^{-1}) and pH (units).

[b] Significant difference ($p < 0.05$) between depths.

[c] Significant difference ($p < 0.05$) between years.

[d] Significant difference ($p < 0.05$) between seasons.

Lim Lake and Frank Lake – Other Water Quality Trends

Inlet Water Quality

Lim Lake

Inlet flow was intermittent based on spring run-off and precipitation events and all samples were collected at the primary inlet at the lake's northwest end (Figure 2, Appendix A). Most water quality parameters had lower concentrations than in-lake values with the exception of DOC, Al, Fe and Si, which were more concentrated, and pH, which was lower (Table 1.12, Appendix B). Cu values were <DL for all inflow samples.

Frank Lake

A majority of the flow entering Frank Lake via the primary inlet at the lake's west end (Figure 3, Appendix A) originated from the effluent discharge from the water treatment plant as well as watershed run-off that mixes with the effluent prior to entering the lake. This resulted in variable water quality and flow volume entering the lake depending on precipitation, melt-water and whether effluent discharge was active or not. Parameters that were most highly concentrated in Frank Lake inflow included sp-cond, TDS, sulphate, total sulphur, Ca, Na, K, Cl, Al, Fe and Zn (Table 1.13, Appendix B). Most parameters were of the highest concentration during 2011 followed by 2013. The 2012 concentrations were the lowest observed during the study however samples were taken outside of the time of effluent discharge during this year. DOC was typically higher at the inlet versus in-lake values while DIC was typically lower. Ca, Na, K, Cl, NO_3, NH_3, Al, Fe and Zn concentrations at Frank Lake's inlet during 2011 all increased in concentration late in the discharge year and after effluent discharge was re-initiated into the lake (discussed more later).

In-Lake Water Quality

During the study, fall turnovers in Lim Lake (max depth=12.0 m) were consistently more complete than spring turnovers. To compare, fall turnovers in Lim Lake occurred to the following depths; 2011 (10.5 m), 2012 (11.5 m) and 2013 (12.0 m), while the spring turnovers in 2012 and 2013 were to 11.0 m and 5.0 m respectively. In Frank Lake (max depth=26.0 m), full water column turnover did not occur in either fall or spring. Fall turnover in the mixolimnion of Frank Lake became more shallow through the study; 2011 (11 m), 2012 (9 m) and 2013 (6 m) while spring turnover occurred to 9 m in both 2012 and 2013.

The occurrence of full water column turnover and breakdown of chemical stability in Lim Lake and only mixolimnion turnover in Frank Lake were main influences on the water chemistry and parameter concentrations measured in each lake. During turnover in Lim Lake, concentrations of major ions and metals would equalize through the water column whereas in Frank Lake, a consistent concentration difference occurred between the mixo- and monimolimnions. In addition, the removal of anoxic conditions in the bottom waters of Lim Lake during turnover changed redox cycling at the sediment-water interface, resulting in concentration fluxes.

The water quality trends of the physical parameters as well as major ions and metals can be found in Appendix A. For Lim Lake, these included temperature, dissolved oxygen, chlorophyll *a*, hardness, Ca, Na, K, Cl, Mg, Ba, Sr, Fe, Mn, Al, Ni, Cu, Zn, Si, TotP, NO_3, NH_3, TKN, alkalinity, pH, DOC, DIC and SO4:TotS ratio, all of which were demonstrated in Figures 1.10–1.36 respectively. For Frank Lake, temperature, dissolved oxygen, chlorophyll *a*, hardness, Ca, Na, K, Cl, Mg, Ba, Sr, Fe, Mn, Al, Ni, Zn, Si, TotP, NO_3, NH_3, TKN, alkalinity, pH, DOC, DIC and SO4:TotS ratio were demonstrated in Figures 1.37–1.63 respectively. A dotted contour line was used in certain figures to represent the Provincial Water Quality Objective (PWQO) for the parameter, thereby illustrating when a particular parameter exceeded the objective.

In order to compare the parameter concentration changes over the study duration, the average concentration through the whole water column in Lim Lake and in the mixo- and monimolimnions in Frank Lake during turnover were calculated. Fall turnover effectively homogenized the water column of Lim Lake and the mixo- and monomilimnions in Frank Lake and therefore, fall served as the best time to compare concentration changes from year-to-year and meromictic stability in both lakes. Tables 1.14 and 1.15 (Appendix B) illustrated these average concentrations and the percent change for Lim Lake (whole water column) and

Frank Lake (mixo- and monimolimnion) respectively between 2011 and 2013. In Lim Lake, the average concentrations of a majority of the water quality parameters at fall turnover decreased from 2011 to 2013. Parameters that increased in Lim Lake were DOC, Al, Cu, Fe, Si and Zn. In Frank Lake, all of the same parameters decreased across the study except for pH, DOC, Si and Fe, which all decreased in both the mixo- and monimolimnions and Al, Mn and Ni which all decreased in the mixolimnion only.

In Frank Lake, samples obtained from 2 m in April 2012, 1 m in February 2013 and 0 m and 3 m in May 2013 showed distinct differences from all other samples. April 2012 2 m sample was higher in Cl, Al, and Fe and lower in sp-cond, Ca, Na, K, Mg and Mo. February 2013 1 m sample was higher in Al and Fe while other parameters such as Ca, Na and Cl showed slight decreases. This Feb 2013 sample was distinctly browner in colour than other samples from Frank Lake. May 2013 0 m and 3 m samples were higher in Al and Fe and lower in Ca, Na, K, Cl, Mg, Mo, Ni and Zn. Zn showed distinct increases in early Oct 2011 from 0-2 m, 9 m and 17-24 m and demonstrated similar increases at similar depths in March 2013 (Figure 1.53, Appendix A). Distinct Zn decreases occurred in late Oct and Nov 2011 as well as in the entire mixolimnion in May-June 2013. Cu was <DL in almost every sample throughout the study (no figure).

Temperature

In both Lim and Frank Lakes, temperature trends throughout all study years were similar, with stable stratification occurring in summer and under the ice in winter (Figures 1.10 and 1.37 respectively, Appendix A). Ice-off was early in 2012, occurring in March, compared to 2013, when it occurred in May. Ice-off in 2013 was rapid, with a major sheet of ice melting in a two-day span. In fall and spring, isothermal conditions occurred for a period of time. Throughout the study, the monimolimnion of Frank Lake was slightly warmer than the overlying hypolimnion. Just prior to ice cover, monimolimnion waters remained at ~4.8°C, ~4.4°C and ~4.3°C below the chemocline in 2011, 2012 and 2013 respectively. This temperature trend is known as dichothermy (Yoshimura 1936*a*, *b*, Yoshimura

1937).

Dissolved Oxygen and Chlorophyll *a*

Dissolved oxygen (DO) was the key parameter for identifying turnover extent in both Lim and Frank Lakes and DO trends in each lake were very different. DO depletion in bottom strata was evident in Lim Lake during summer and winter stagnation, however, replenishment of DO to these anoxic strata occurred during fall and partially in spring (Figure 1.11, Appendix A). In Lim Lake, DO replenishment was more complete in fall than spring and spring 2012 replenishment was more complete than spring 2013. DO replenishment in Frank Lake to the anoxic, bottom strata did not occur at any point in the study (Figure 1.38, Appendix A).

In general, DO demonstrated clinograde trends during stratification in both lakes, however, heterograde trends were observed periodically. During summer 2011, a positive heterograde curve (maximum DO concentration) was observed from 2-5 m in Lim Lake. Heterograde trends in Frank Lake by definition were negative but could have also been classified as positive. Regardless, these heterograde trends in Frank Lake were observed during July 2011 (2 m), March 2013, April 2013 and August 2013 (all 4-6 m). DO was higher above and below these depths.

Chl *a* concentrations in Lim and Frank Lakes coincided roughly with DO heterograde peaks but not in all situations. The positive heterograde DO curve in Lim Lake coincided with a maximum chl *a* concentration in the water column (Figure 1.12, Appendix A) however, other chl *a* peaks were observed and did not coincide with an increase in DO. In Frank Lake, maximum chl *a* concentration depths did not coincide perfectly with DO heterograde peak depths but some temporal overlap occurred (Figure 1.39, Appendix A). No phytoplankton biomass data was available to support these DO and chl *a* trends but live specimens of *Daphnia sp.* and *Chaborus flavicans* (Figure 1.64, Appendix A) were found under the ice in April 2013 in samples near the surface and at 11.0m respectively, indicating zooplankton presence in the Frank Lake.

Specific Conductance and Total Dissolved Solids

Like DO, sp-cond (corrected to 25°C) was a key parameter for identifying turnover extent and meromictic stability in both Lim and Frank Lakes (Figures 1.65 and 1.66 respectively) as well as the mixo-, chemo- and monimolimnion depths in Frank Lake. Laboratory TDS trends in Lim and Frank Lakes (Figures 1.67 and 1.68 respectively) closely matched trends demonstrated by field sp-cond.

Average sp-cond and TDS concentrations at fall turnover in Lim Lake decreased by 47% from 2011 to 2013 (Table 1.14, Appendix B). In Frank Lake, decreases of sp-cond and TDS from 2011 to 2013 in the mixolimnion were 26.9% and 29% respectively and 8.8% and 18% in the monimolimnion respectively (Table 1.15, Appendix B). Comparison of the whole year averages of sp-cond and TDS in Table 1.5 also demonstrated the decrease from 2011 to 2013.

In Frank Lake, double chemoclines occurred in spring and summer seasons. The shallow chemocline, occurring in the mixolimnion, corresponded roughly to temperature stratification and followed the metalimnion trend. The deep chemocline formed the separation of the mixo- and monimolimnion and was located just below the hypolimnion. During fall, the shallow chemocline in the mixolimnion deteriorated and only the deeper chemocline persisted into winter.

Unique sp-cond trends occurred in the mixolimnion during fall 2011. As mentioned above, after deterioration of the shallow chemocline, isohaline conditions existed in the mixolimnion, however, the sp-cond measured during these isohaline conditions increased from early October to November. Maximal peaks of sp-cond occurred at 7m (2000 $\mu S\ cm^{-1}$) during early October (Oct 5, 2011) and at 9 m (2150 $\mu S\ cm^{-1}$) in late October (Oct 26, 2011) in the mixolimnion. Figure 1.73 (Appendix A) clearly demonstrated these sp-cond peaks. As turnover continued, these peaks disappeared and by Nov 16, 2011 the mixolimnion reached its maximum depth of 11 m for 2011 and peaks were absent. These sp-cond peaks occurred in conjunction with concentration increases in major anions and metals including total sulphur and sulphate (Figures 1.71 and 1.72 respectively) as well as Ca, Na, K, Cl, NO_3, NH_3, Al, Fe and Zn (all Figures in Appendix A). During 2011, effluent discharge into Frank Lake ceased from August 29th to September 19th (Figure 1.74, Appendix A). The re-initiation of effluent discharge into the lake occurred 16 days prior to the first sp-cond peak in Frank Lake in early October 2011. The reinitiated effluent discharge flow volume was similar to earlier in 2011 (Figure 1.74, Appendix A), however, the same parameters listed above that had concentration peaks in the Frank Lake mixolimnion also had increased concentrations in the reinitiated effluent discharge (Figures 1.75 – 1.77, appendix A). The two concentration increases were clearly linked.

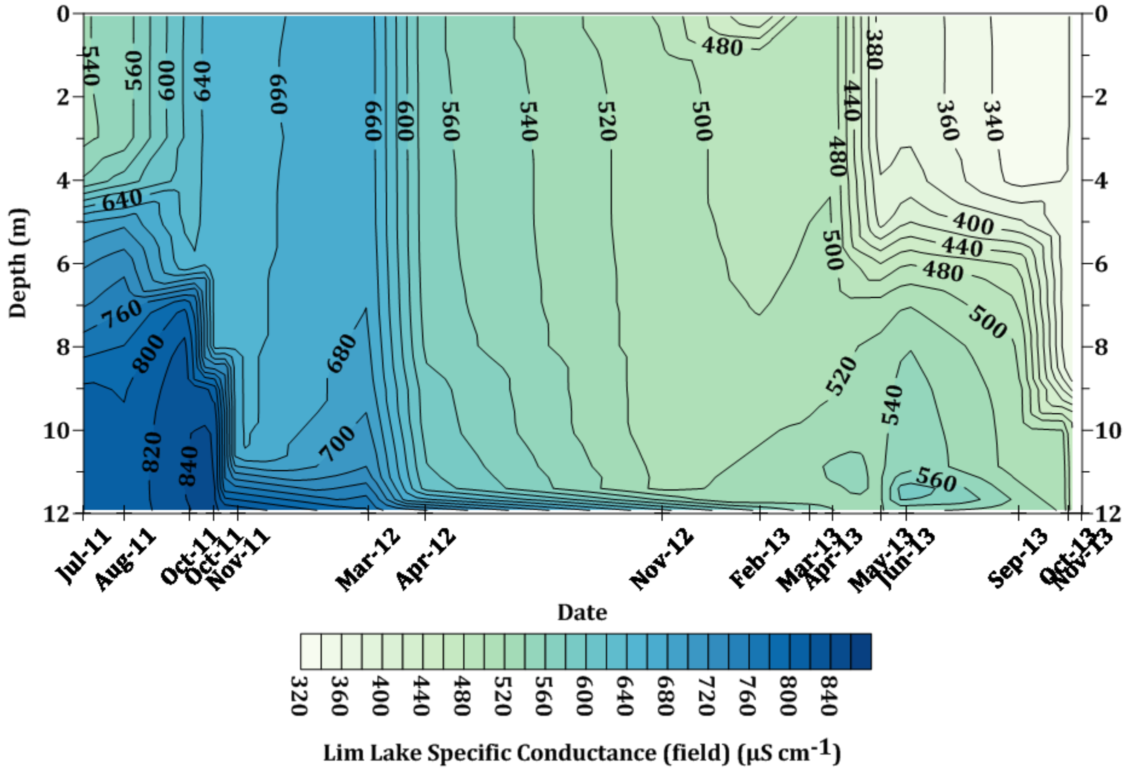


Figure 1.65. Lim Lake specific conductance (µS cm^{-1}) multi-probe profiles, Jul 2011-Nov-2013.

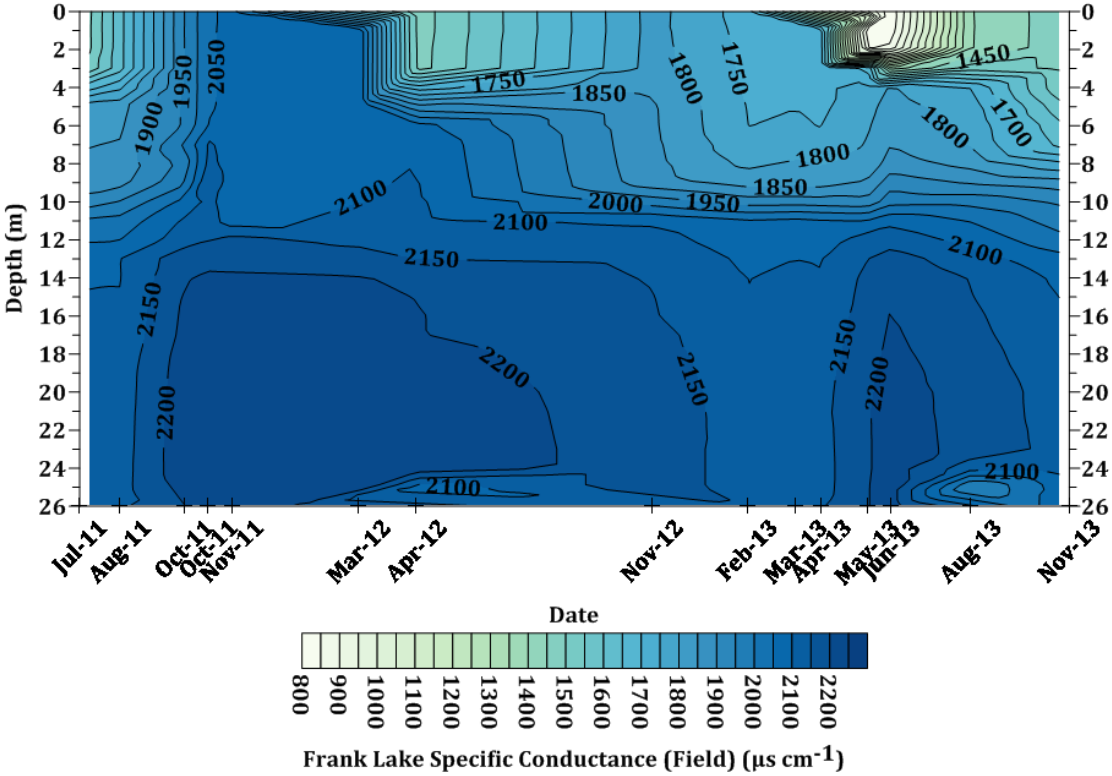


Figure 1.66. Frank Lake specific conductance (µS cm^{-1}) multi-probe profiles, Jul 2011-Nov-2013.

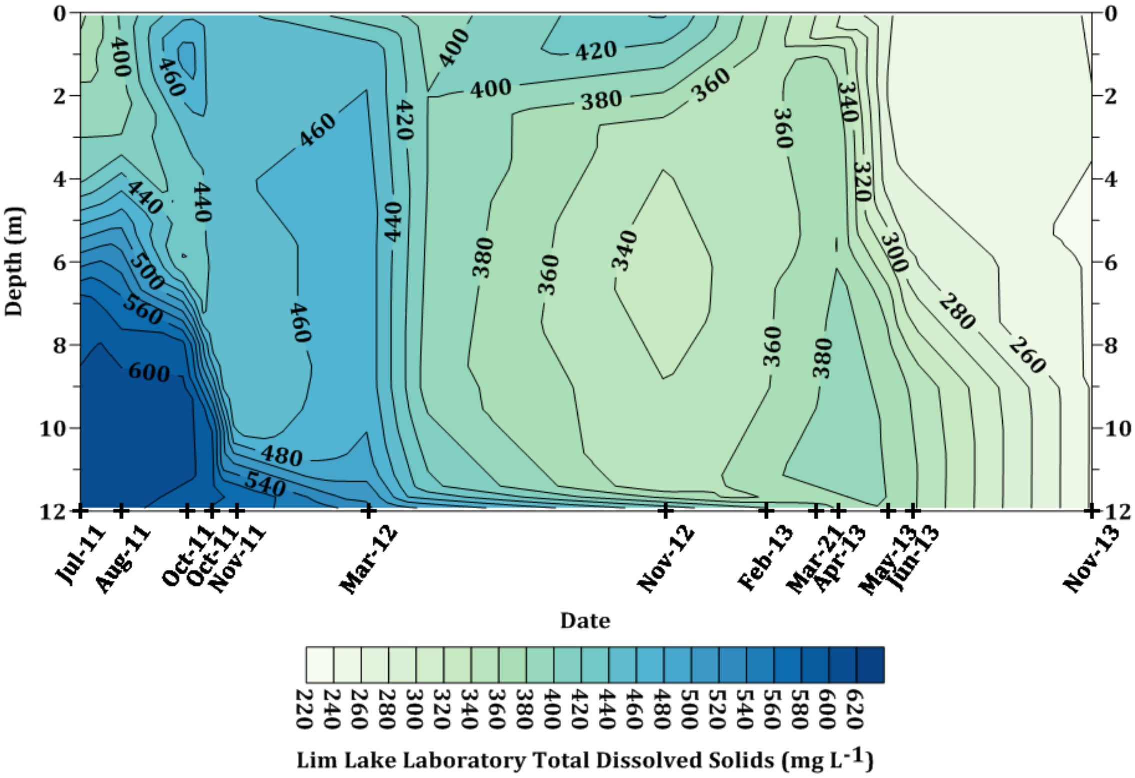


Figure 1.67. Lim Lake total dissolved solids (mg L^{-1}) laboratory analysis from Jul 2011-Nov 2013.

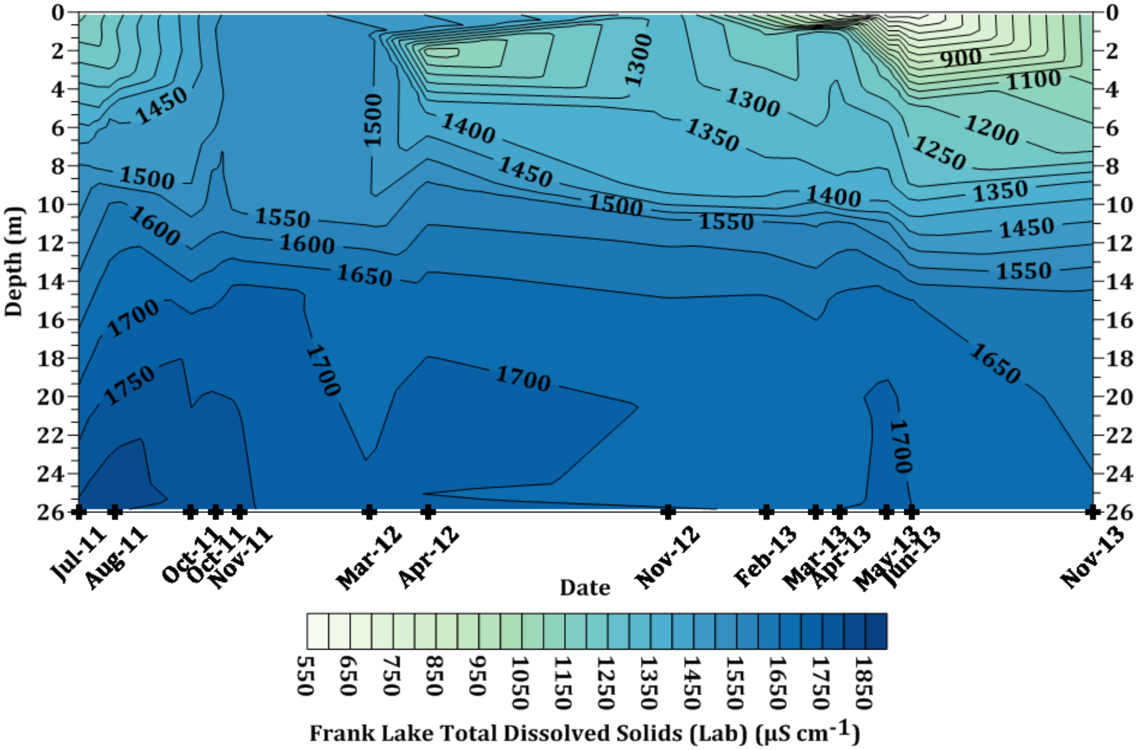


Figure 1.68. Frank Lake total dissolved solids (mg L^{-1}) laboratory analysis from Jul 2011-Nov 2013.

Sulphur Compound Characterization

Total sulphur and sulphate were the only sulphur species identified during the study in both lakes and were the most highly concentrated ions measured. Sulphite (SO_3^{2-}), thiosulphite ($S_2O_3^{2-}$) and sulphide (S^{2-}) were analyzed but were below detection limits (<DL) in all samples. In general, total sulphur and sulphate concentrations increased with depth throughout the study in both lakes, except for during periods of full water column turnover in Lim Lake. Sulphate values were equivalent or higher than total sulphur values throughout the study. Other lake-specific trends are discussed below.

Lim Lake

For a brief period of time in summer 2011, both total sulphur (Figure 1.69) and sulphate (Figure 1.70) had a lower concentration in bottom strata than in the mid-lake strata. These decreases disappeared in the fall. A substantial increase in total sulphur and sulphate occurred during late October 2011 throughout the water column. After this increase, both parameters substantially decreased and were more stable through the water column for the remainder of the study. Sulphate demonstrated slight decreases during winter months. The average concentration of total sulphur and sulphate at fall turnover decreased 59.30% and 69.34% from fall 2011 to fall 2013 respectively (Table 1.14, Appendix B). The ratio of total sulphur to sulphate for each sample was close to or slightly above 1 throughout the study (Figure 1.36, Appendix A). Ratios <1 occurred in bottom waters during summer 2011 as well as during late fall 2011. A ratio of exactly 1 represented equivalent amounts of total sulphur and sulphate in a sample.

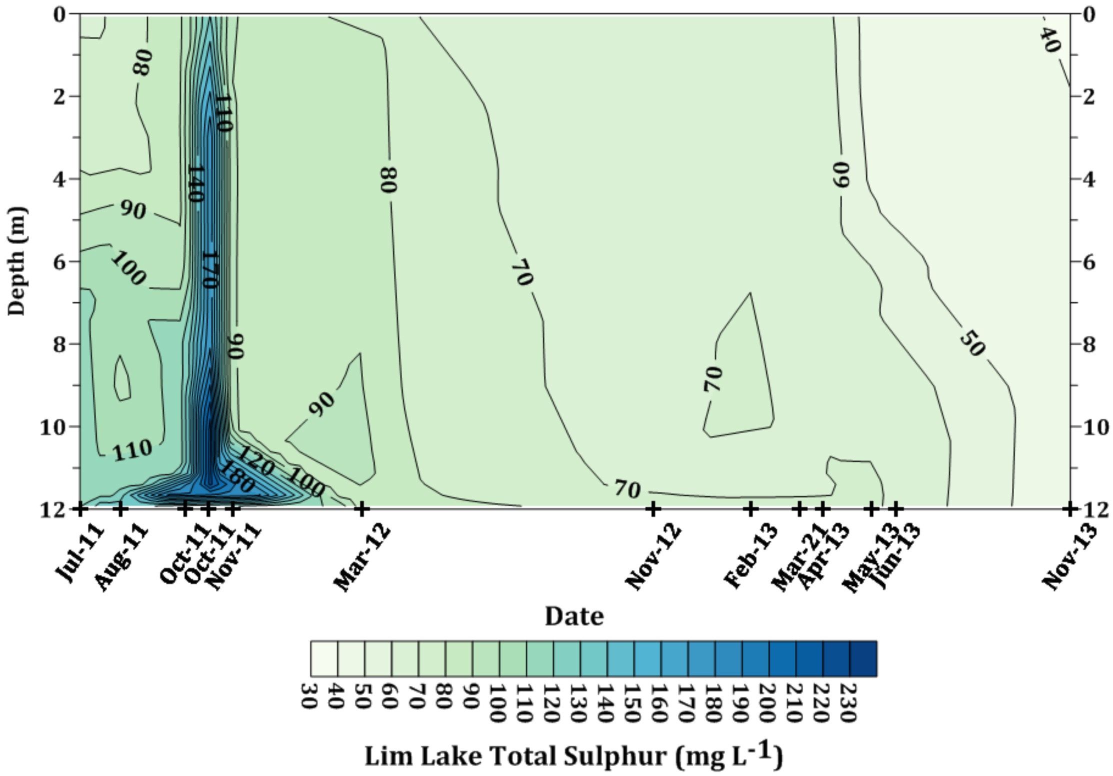


Figure 1.69. Lim Lake total sulphur (mg L^{-1}) profiles from Jul 2011-Nov 2013.

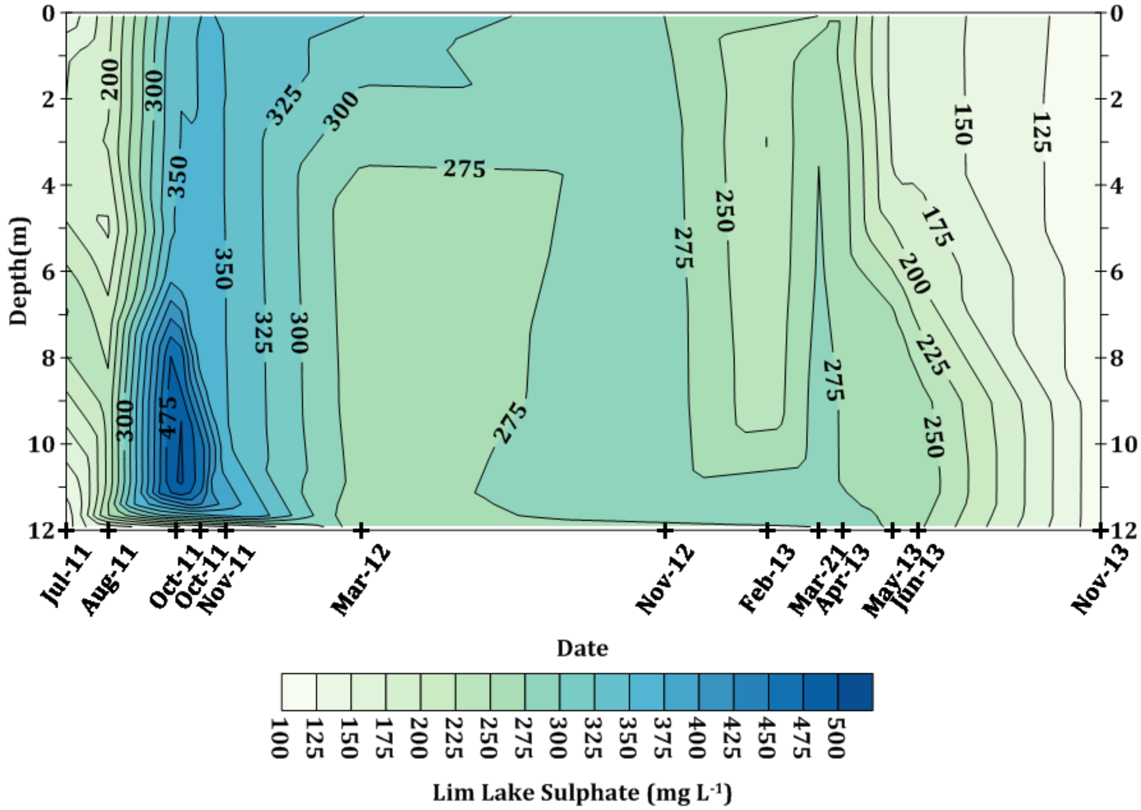


Figure 1.70. Lim Lake sulphate (mg L^{-1}) profiles from Jul 2011-Nov 2013.

Frank Lake

Total sulphur (Figure 1.71) and sulphate (Figure 1.72) concentrations were consistently higher below the chemocline. A substantial increase in total sulphur and sulphate occurred during October 2011 but by November 2011, concentrations had lowered. A similar increase in sulphate occurred in fall 2012. Winter sampling identified decreased sulphate concentrations from the fall previous. Notable surface decreases in total sulphur and sulphate occurred during both spring 2012 and 2013 with the greatest decrease in sulphate concentration was down to 68 mg L^{-1} at 0 m in June 2013. The decrease occurring in spring 2013 was not sustained but its effect was noticeable at the surface into the summer. Average total sulphur decreased by 31.8% and 26.7% in the mixo- and monimolimnions respectively from fall 2011 to 2013 (Table 1.15, Appendix B). Average sulphate decreased by 56.3% and 47.8% in the mixo- and monimolimnions respectively from fall 2011 to fall 2013 (Table 1.15, Appendix B).

Total sulphur to sulphate ratios were ~1 for a majority of the study (Figure 1.63, Appendix B). Notable times when the ratio was <1 were during summer 2011 and in spring and summer 2013 in surface strata. The ratio was >1 during fall 2011 throughout the whole water column but typically was only observed in bottom strata.

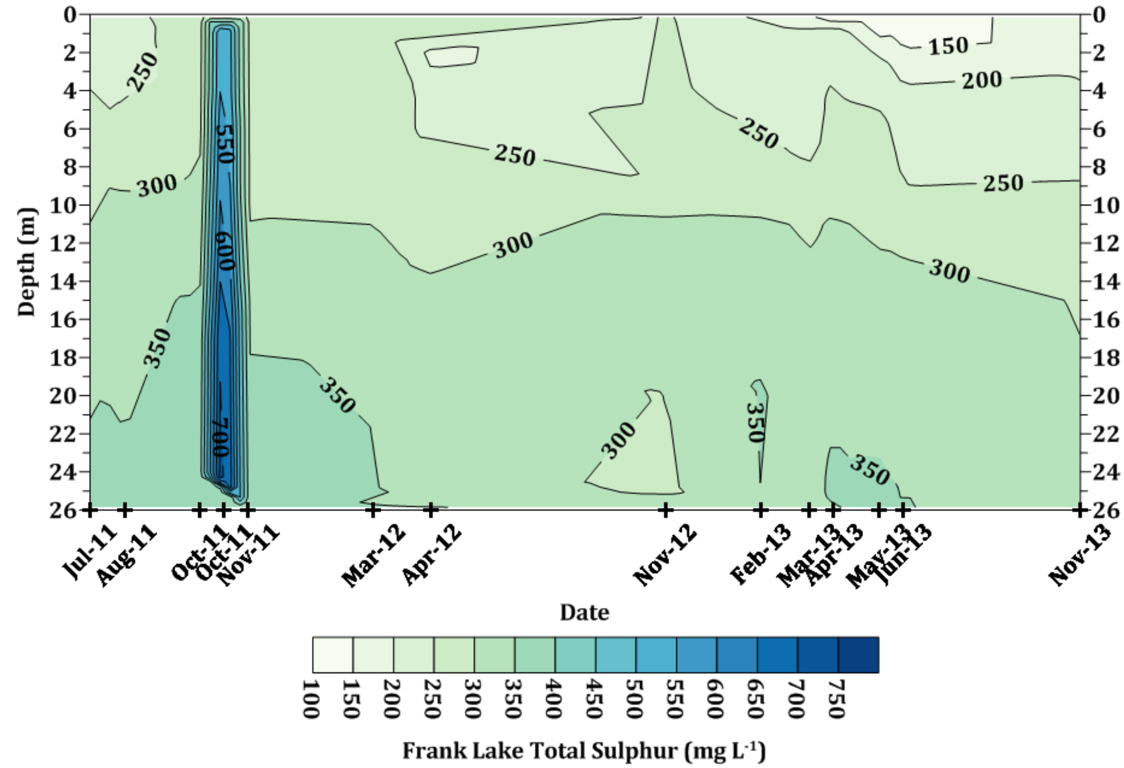


Figure 1.71. Frank Lake total sulphur (mg L^{-1}) profiles from Jul 2011-Nov 2013.

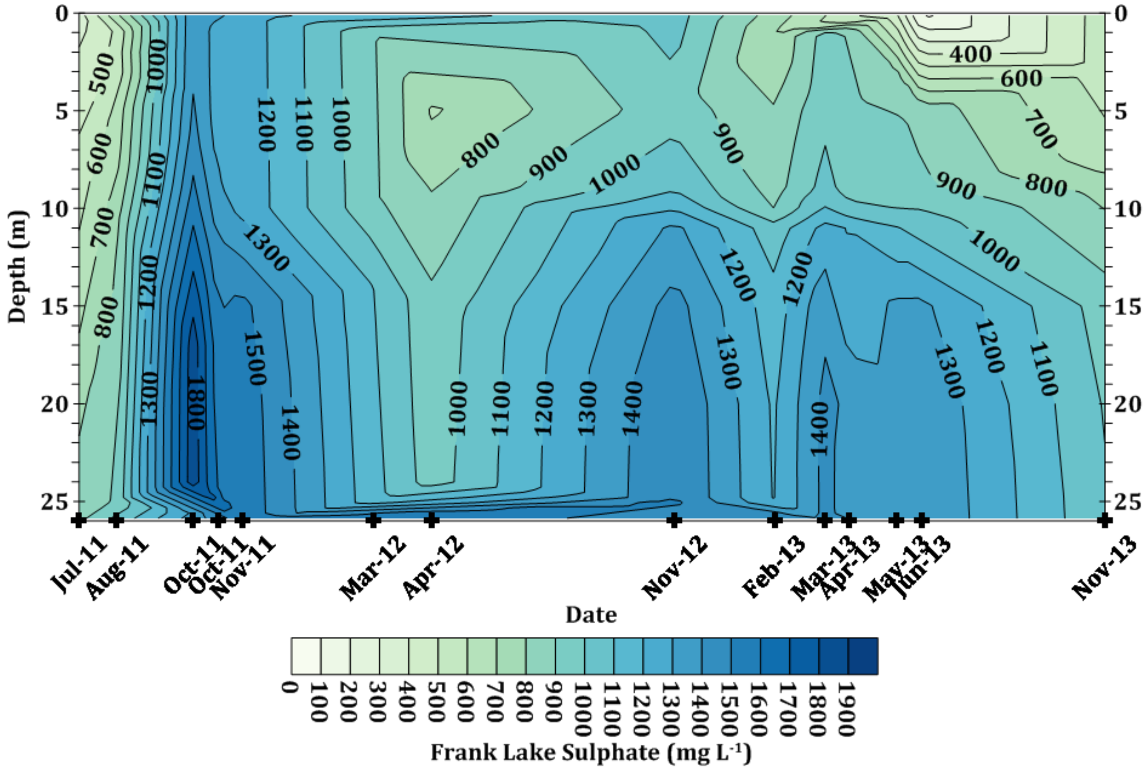


Figure 1.72. Frank Lake sulphate (mg L^{-1}) profiles from Jul 2011-Nov 2013.

Rain Event

Both Lim and Frank Lake experienced a large rain event during the time of sampling in May 2013. Approximately 44.5 mm of rain fell over 2 days and had an immediate and long term effect on both the in-lake and inflow water quality in both study lakes. This was the largest rain event measured in the study.

Comparison to Spangle Lake (Reference Lake)

Only two data sets were acquired for Spangle Lake during the current study in August 2011 and March 2012. Similar to observations made by consultants in previous years, oxygen depletion through the water column was observed in both of these sample sets along with stable thermal stratification (Figure 1.78, Appendix A). In addition, sp-cond was constant from the surface to the bottom of Spangle Lake during both of these sample sessions, indicating that chemical stability in the lake is completely absent (Figure 1.79, Appendix A). Chl *a* concentrations in Spangle Lake were comparable in magnitude to Lim and Frank Lakes (~1.5-2.5 μg L^{-1}) and the characteristic concentration spike at depth that occurred in Lim and Frank Lakes also occurred at 2 m during August 2011 in Spangle Lake (Figure 1.78, Appendix A). Concentrations of all parameters, especially those contributing to TDS, were all markedly lower in Spangle Lake compared to the study lakes (Table 1.3, Appendix B).

Discussion

Lim Lake and Frank Lake – Turnover Extent and Meromictic State

The results showed that the two lakes differed in the extent and occurrence of circulation within their water columns.

Lim Lake

The trends of many parameters suggested that Lim Lake was not meromictic but rather could be considered monomictic, meaning it has one complete turnover per year. This one complete annual turnover occurred during the fall of each study year. Both thermal and chemical stability were absent during fall for a long enough time for wind to promote a turnover event that encompassed the entire water column of Lim Lake. The presence of constant temperature, DO, sp-cond and ion/metal concentrations during each fall were the main indicators that the meromictic stability observed in the 2008 EEM study (Weech and Orr 2009*a*) had begun to deteriorate.

The nearly complete turnover in spring 2012 supported this conclusion and suggested that Lim Lake might even be dimictic once again. However, the incomplete turnover of spring 2013 indicated that Lim Lake was still not free of meromictic stability. The chemical stability still present in Lim Lake was enough to limit full spring turnover. It has been observed in lakes with elevated dissolved solids, such as Lim Lake, that chemical stability that is carried over from fall or develops over the stagnant winter months can prevent mixing in spring (Hutchinson 1957, Wetzel 2001, Wetzel *et al* 1972). If this chemical stability is further enhanced by early/rapid thermal stratification at the surface due to a warm or late spring, turnover in spring will be inhibited since the wind will not have had sufficient time to mix the water column (Hutchinson 1957). Such periodic incomplete turnover was observed in the spring in Lawrence Lake, Michigan and the fall in Crooked Lake, Indiana (Wetzel 2001, Wetzel *et al* 1972). During the current study, both springs were rapid and warm and helped to support this theory.

Decreases in many parameters occurred in Lim Lake over the study duration since the lake was now free from the influence of effluent and it is expected that this trend will continue as each successive year brings the lake back to near-background levels. It is possible that increased concentrations of parameters in the sediment that have resulted from effluent discharge may continue to influence the water column in Lim Lake, especially if anoxic conditions continue to occur during winter, spring and summer and redox cycling is promoted. Again, since the study occurred in such close proximity of the lake transitioning from meromictic to monomictic and eventually dimictic, the long term seasoning cycling that will likely reach equilibrium in the lake had not yet been established. As the lake approaches background levels of most parameters, more consistent annual chemistry trends will result. Another key observation was that even after the large rain event in May 2013, Lim Lake was still able to turnover in the fall of that year despite heavy dilution of its surface waters.

Frank Lake

During the current study, Frank Lake's chemical stability was strong and persistent and Frank Lake could be classified as meromictic. Presence of a chemocline and an anoxic monimolimnion with elevated concentrations of nearly all parameters supported this statement. However, the mixolimnion turnover in Frank Lake was not static and variability of turnover depth occurred, particularly during fall. Fall turnover became shallower as the study progressed moving from 11 m in 2011, to 9 m in 2012 and 6 m in 2013. The year-to-year meromictic stability and turnover in Frank Lake will continue to vary depending on precipitation events during open-water periods, effluent discharge volume/water quality and meteorological conditions at the time of turnover. Inputs of large volumes of low salinity water from rain or snowmelt accompanied by low winds will minimize turnover in Frank Lake by increasing the difference in salinity between the mixo- and monimolimnions and ultimately increasing the overall chemical stability through the lake's deep water column.

Chemical Parameter Variations

The results of the cluster analyses, ANOVAs and isopleths identified parameters that varied similarly, both spatially (layers) and temporally (year and season), with a high or low level of significance. However, not all parameters were controlled by the same mechanisms. The main assumptions of the ANOVA include; the probability distribution of the data is normal, the observations are sampled randomly and independently of each other and the variances of the populations are the same (Lunney 1970). Data is said to be parametric when it fits these criteria. If the data does not meet these assumptions it is considered non-parametric and other statistical techniques such as a Kruskal-Wallis test should be used. Log-transformation and normalization of data can allow it to satisfy the assumptions of the ANOVA and other parametric tests such as *t*-tests (Zuur *et al* 2010, O'Hara and Kotze 2010).

Lim Lake – Monomictic

Parameters Elevated In Bottom Strata

The clusters resulting from Lim Lake's 2011 and 2013 data were illustrated in Figures 1.6 and 1.7 respectively. Lim Lake was in the process of natural remediation during the study and this had a main influence on the results of the statistical analyses. Ions and metals largely contributing to the TDS of the lake (Ca, hardness, total sulphur, K, Na, Sr, Mg, sp-cond, sulphate, Cl, Zn, Ni, Ba, Fe, alkalinity, Mn, TKN and DIC) demonstrated the highest concentrations in bottom waters during summer 2011 and were still elevated but to a lesser extent in bottom waters during winters and summer 2013. The turnover events resulted in a decrease and equalization of these parameters through the water column. Ca, hardness, K, Na, Sr, Mg, Cl, Ni, Ba, alkalinity and TKN were all elevated in bottom strata prior to turnover events, not necessarily due to their enhanced solubility in anoxic conditions, but due to their propensity to settle overtime. All of these parameters excluding Zn (discussed later) and Ni, which tended to vary more independently in the water column, increased and decreased sporadically and were found to vary significantly between layers as indicated by the ANOVA (Table 1.4).

Other parameters that were elevated in bottom strata prior to turnover, such as Fe and Mn, were predominantly controlled by redox conditions/cycling influenced by anoxic conditions (Hamilton-Taylor *et al* 1996, Hongve 1980, Hongve

1997, Mortimer 1941). Fe was likely sourced from the sediments in the form of reduced, soluble complexes, which is a typical occurrence in anoxic conditions (Hamilton-Taylor *et al* 1996, Hongve 1980, Hongve 1997, Mortimer 1941). Return of turnover to the lake in fall 2011 oxidized the reduced/solubilized ferrous iron into oxidized/precipitated ferric complexes such as ferri-silico-humate or $Fe(OH)_3$ (Mir and Kachroo 1982, Mortimer 1941). Regarding Mn; some of the increased Mn in bottom strata during anoxic conditions was likely sourced from the sediment but a small amount of Mn in the anoxic bottom waters was potentially sourced from the epi- and metalimnions, where Mn slowly oxidized/precipitated, settled and then reduced/solubilized in the hypolimnion (Balistrieri *et al* 1992, Davidson 1981, Davidson 1993, Davidson *et al* 1982, Hangrove 1980, Hongve 1997). The slow oxidation of Mn was demonstrated by the maintenance of higher Mn in oxidized waters and a slight Mn gradient during April 2012, where turnover occurred efficiently down to 10.5 m. The lowering of Mn in the epilimnion during summer months could have been due to either this slow oxidation principle or dilution from heavy rain events, such as the one that occurred in May 2013.

Some of the parameters that contributed to TDS and increased with depth during stratification (DIC, Cl, sulphate and total sulphur) also increased throughout the whole water column during the fall 2011 turnover event (Figure 1.6, Cluster 2). These increases could have only been sourced from the anoxic bottom waters and sediment since effluent discharge into the lake had ceased. The form of sulphur in water is largely controlled by pH, Eh and oxygen concentration (Cook 1982, Davison and Heaney 1978, Hem 1960*a*, *b*, Hem and Cropper 1959, Hem and Skougstad 1960, Jørgenson 1990, Urban *et al* 2001). The influx of oxygen to the lake bottom during this turnover likely oxidized and mobilized some of the sulphur that had been precipitated and removed from the water column as H_2S, FeS etc. during prolonged anoxia (Carignan and Tessier 1988, Giblin *et al* 1990, Kling *et* al 1991, Rudd *et al* 1986, Nriagu and Soon 1985). It is possible that this was the first full turnover event to occur in Lim Lake since the first observation of meromixis in 2008 (Weech and Orr 2009*a*), which is why such great increases in the water column of these parameters were observed. The decrease in sulphate concentrations that occurred during winter months indicated that sulphur reduction and allocation to the sediments was likely occurring during the return of anoxic conditions under the ice. No pore water or sediment data was sampled to support this theory. The allocation of sulphur to the sediments as organic and inorganic forms was a likely mechanism that aided in the lowering of sulphate and ultimately TDS in Lim Lake and promoted deterioration of meromixis.

To better understand the increase in sulphur compounds during the fall 2011 concentration spike, a ratio of total sulphur to sulphate was developed to discover the proportion of sulphate contributing to the total sulphur concentrations (Figure 1.36, Appendix A). The <1 ratios observed in late October 2011 indicated the presences of other forms of sulphur other than sulphate. Note that the low ratios in bottom waters during summer 2011 were likely for the same reason. Since thiosulphite and sulphite were <DL for these samples, it is likely that sulphur was in the form of either H_2S (not tested) or organic complexes such as CH_3–S–CH_3, CH_3-–S–S–CH_3, CH_3–S–C_2H_5, CH_3-CH_2CH_2–SH etc. (Puacz W *et al* 2001) or sulphur esters in the water column. Ion chromatography measurement of sulphate does not destroy these organic compounds in the same way that inductive coupled plasma measurement of total sulphur does (Edwards *et al* 1992). So, this was one potential reason for the <1 ratio in summer 2011 and early October 2011. Accumulation of sulphur in anoxic water and sediment is typical in high-sulphur lakes (Baker *et al* 1992). Sulphur has been accumulating in the Lim Lake sediments as a result of effluent discharge based on sediment sulphur levels of 4700-15000 mg kg^{-1} observed previously (Beak International Incorporated 2000*b*) and so, a great deal of sulphur is available for mobilization to the water column. After the fall turnover event of 2011, both total sulphur and sulphate had slightly increasing gradient with depth during stratification periods but to a much lesser magnitude which was why the ANOVA did not indicate that they varied significantly between layers (Table 1.4).

Parameters elevated in bottom strata that were eliminated almost completely from the water column during turnover were ammonia, Si and TotP

(Figure 1.6, Cluster 3). Oxidation of all of the ammonia to nitrate during turnover was the likely cause for such a decrease (Keeney 1973). Ammonia in deep, low oxygen waters can be sourced from the sediment, organism excretion or organic decay (ammonification) (Keeney 1973). No summer 2013 ammonia data was available for comparison to summer 2011. After summer 2011, ammonia concentrations continued to decrease throughout the study and were not as dynamic as nitrate's.

Although Si data was only available up until June 2013, some characteristic trends were observed. Summer decrease of Si that occurred in epilimnion waters was likely a result of phytoplankton harvesting and then subsequent population death in the fall causing release of this Si back into the water column (Mir and Kachroo 1982, Mortimer 1941, Munawar and Munawar 1975).

Parameters Elevated in Surface Strata

Some parameters demonstrated higher concentrations in surface strata (Figure 1.6, Cluster 4: temp and pH, Figure 1.7, Cluster 5: DO, NO_3 and Cu). All of these except NO_3 demonstrated a significant level of layer variance from the ANOVA. The presence of temp and DO in this cluster is logical since surface strata remain warm and well oxygenated for much of the year compared to the bottom strata. NO_3 is the most common form of oxidized nitrogen and often is more elevated at the surface during anoxic conditions (Keeney 1973). One exception from this NO_3 trend occurred during May and June 2013 when nitrate increases expanded throughout the whole water column. The initial increase at the surface in May, which then continued into bottom waters in June, indicated that the increase might have been linked to the heavy rain event of May but nitrate inflow into the lake was not excessively concentrated during this month (0.058 mg L^{-1}), indicating that the nitrate was internally sourced. The amount of nitrogen sourced from the atmosphere by nitrogen-fixing bacteria is variable depending on the available concentration of nitrogen available to these organisms in the water column (Flett *et al* 1980). It is possible that nitrate originating from nitrification in the littoral-zone sediments due to wind mixing could be the source. Nitrite was <DL for the entire

study except for the near-bottom samples taken in May (0.028 - 0.032 mg L^{-1}) indicating that nitrification at the sediment surface was occurring. The lake was already sufficiently stratified by this time so exchange between epi- and hypolimnion waters was likely minimal but it is possible that combined effects of wind, rain temperature and rain TDS influenced stratification destabilization within the lake and allowed some vertical diffusion to occur. The profiles obtained are only a snap-shot in time and so exact lake dynamics in relation to the rain event are uncertain. A congruent decrease in ammonia in bottom waters was observed during the rain event indicating that it could have contributed to some of the nitrate increases.

Cu decreases observed in the hypolimnion were likely the result of co-precipitation or adsorption onto settling organic matter (Riley 1939). The elevated levels of Cu at Lim Lake's surface were not sourced from the inlet where all samples measured <DL. This indicated that Cu in the lake must have been sourced either from the sediment, precipitation, groundwater, run-off at another area of the lake (potentially off of the north-shore ridge separating Lim Lake and the tailings) or from decay of phytoplankton, which had had Cu accumulated as micronutrients in their cells (Riley 1939, Hamilton-Taylor *et al* 1996).

Parameters Varying Uniquely

Parameters showing unique variability at points in time during the study included TKN, Zn DOC, chl *a* and Al (2011) as well as ammonia, Si and TKN (2013). TKN demonstrated little change in surface waters but was usually more concentrated in bottom strata indicating that a large portion of it was sourced to ammonia. The increases of Zn at 3 m, 6 m and 9 m during early October 2011 could be linked to phytoplankton decay dynamics in the epilimnion and the fact that oxidized forms of Zn are typically insoluble (Hamilton-Taylor *et al* 1996). DOC was relatively constant through the water column early in the study and increased in surface strata following the rain event. Chl *a* will be discussed later. Al and Si both showed few constant trends throughout the study. Slightly higher concentrations with depth occurred with sporadic increases and decreases in the upper strata that were largely variable.

Rain Event of May 2013

The large rain event in May 2013 resulted in a substantial decrease of many of the TDS-contributing parameters in surface waters and this decrease carried through into the summer and fall turnover of 2013 (Figure 1.7, Cluster 1: Ca, hardness, total sulphur, K, Na, Sr, Mg, sp-cond, sulphate, Cl, Zn, TDS, Ni, Ba, Fe, alkalinity, Mn, TKN and DIC). Sulphate remains to be the highest elevated of these ions in Lim Lake. The significant levels of variability that occurred between years for many of these parameters was largely enhanced by this rain event since it created a greater divide in water quality from earlier in the study. Dilution via precipitation and run-off has been and will continue to be the main mechanism by which Lim Lake's water quality improves, since this lake is at the headwaters of the watershed and surface inflow is sporadic and only contributes small volume inputs to the lake. Only Al, TotP and DOC increased in surface waters as a result of the rain event. DOC, Al, Fe, Zn and Si all demonstrated average concentration increases at the time of turnover from 2011 to 2013 (Table 1.14, Appendix B) and it was likely that effluent discharge actually diluted these parameters in Lim Lake. As the lake remediates, concentrations will return to background levels (Table 1.1, Appendix B). All of these parameters except Zn demonstrated higher concentrations at the inlet (Table 1.12, Appendix B) indicating the influence of the surrounding watershed geology on these parameters. Cu also demonstrated and increase over the study but the increase was very minimal.

Frank Lake – Meromictic

Typical redox trends in Frank Lake were not quite as obvious as in Lim Lake. The influence of effluent on Frank Lake made it difficult to discern concentration fluctuations due to effluent and dilution from rain and snowmelt versus redox conversions or biological cycling. In general, a majority of the results of the clustering and ANOVA exercises were influenced in large part by the effluent and natural input dilutions.

Effluent Discharge Effects

In Frank Lake, most parameters were elevated in the bottom strata of the monimolimnion as indicated by the dominance of Cluster 1 in both 2011 and 2013 (Figures 1.6 and 1.7 respectively). In general, most of these parameters have settled to the bottom of Frank Lake as a result of decades of effluent discharge. The re-initiation of effluent discharge on September 20, 2011 after being stopped on Aug 31, 2011 formed the basis of the clustering patterns of 2011. Many of the water quality parameters of Cluster 1 increased in concentration throughout the water column of Frank Lake after effluent discharge re-initiated including TDS (Figure 1.68), sp-cond (Figure 1.66), total sulphur (Figure 1.71) and sulphate (Figure 1.70). Inlet water quality into Frank Lake after re-commencement of effluent discharge demonstrated increases in sp-cond, TDS, total sulphur and sulphate (Figure 1.75, Appendix A), Ca, Na, K, Cl, NO_3 and NH_3 (Figure 1.76) as well as Al, Fe, Zn, Si, DOC and Mg (Figure 1.77). It is known that inflows of a higher density than the receiving waterbody they enter (whether from temperature or salinity) will plunge until they meet their equal density within the lake (Hogg *et al* 2013, Imberger and Hamblin 1982). This plunging phenomenon was what resulted in these water quality changes within Frank Lake.

Mn increased with depth beginning below the monimolimnion (Figure 1.50, Appendix A). As mentioned, Mn is insoluble in oxidized form which explains the lowered mixolimnion concentrations during turnover. The precipitated Mn falls towards the monimolimnion slowly passing through the chemocline and re-dissolving as it is reduced in the anoxic conditions (Balistrieri *et al* 1992, Davidson 1981, Davidson *et al* 1982).

Lowered DIC during fall 2011 turnover may have resulted from co-precipitation of DOC with Fe oxidation (Hongve 1997). Harvesting of CO_2 from the epilimnion by phytoplankton was a likely cause of DIC depletion during summer and release of DIC from the sediments during anoxic conditions as carbon dioxide or bicarbonate was the likely cause during summer months (Hutchinson 1941).

Cluster 2 (chl *a*, Si and DOC) and Cluster 4 (NO_3, Cl, ammonia and Mg) in

2011 formed as a result of the same effluent discharge event discussed above. The effluent contributed to dilutions of the parameters of Cluster 2 in the whole water column and elevated the parameters of Cluster 4 at the surface. Prior to fall, these parameters did not have a strong concentration change with depth. Concentrations of Si and DOC in the re-initiated effluent (Figure 1.77, Appendix A) did not increase in concentration as appreciably as NO_3, Cl, ammonia and Mg did (Figure 1.76, Appendix A). The ANOVA results also reflected the results of these cluster patterns. Chl *a*, DOC, Mg and Cl were all parameters that did not demonstrate significant variation between layers throughout the study (Table 1.4).

Cluster 3 parameters (DO, Sr, temp and pH) were not affected by the effluent discharge event. Sr is the only parameter that would have been expected to vary from the effluent but its concentration in the effluent did not increase greatly after discharge re-initiation (Figure 1.77, Appendix A). The fact that Sr had a much lower concentration below the chemocline throughout the study (Figure 1.47, Appendix A) indicated that some sort of removal mechanism of this parameter was occurring, either from biological harvesting or chemical mechanisms.

Effect of Rain Event

The rain event in May 2013 gave a brief snapshot in time of what sort of water chemistry might be expected in the Frank Lake if it were allowed to remediate naturally and if effluent discharge were absent. Parameters that were diluted during the rain event of May 2013 indicated that they have an elevated concentration in the lake as a result of effluent. The parameters that increased in concentration have likely been diluted by effluent and their concentrations will likely increase once again after discharge ceases. The parameters that increased in these samples were chl *a*, DOC, Al and Fe and excluding chl *a* (discussed later), surface concentrations after the rainfall were a representation of the typical background concentrations observed in natural run-off from the watershed (Table 1.2, Appendix B) (SENES Consultants Limited 1984). Frank Lake's inflow passes through a swamp-like area, which may allow it to accumulate elevated amounts of DOC and bound Al and Fe.

In addition to the dilution or concentration-increase effect of the rain, clustering trends were also dictated by the how surface and bottom concentrations changed throughout the summer after effluent discharge commenced. The dilution effect was maintained to an extent by the parameters found in Cluster 1 of 2013. By fall 2013, some of these parameters returned to concentrations observed earlier in the year (alkalinity, Mn, Fe and Ba) while some, and even after a whole summer of effluent discharge, did not (Ca, hardness, total sulphur, K, Na, Sr, Mg, sp-cond, etc.). For example, the alkalinity in 1985, prior to mine influence was 7.9 mg L^{-1} (SENES Consultants Limited 1984) and so the alkalinity depletion down to 16 mg L^{-1} during the precipitation event of May 2013 was approaching the background concentration (Table 1.2, Appendix B). A 30 mg L^{-1} concentration had returned by fall 2013. On the other hand, the parameters of Cluster 3 (Si, Zn, Mn, Ni and TotP) were diluted by the rain but had begun to return to typical concentrations from earlier in the year by June 2013. The concentration increase effect was maintained by some parameters of Cluster 4: Al and Fe.

Parameters Varying Uniquely

Fe dynamics at the bottom of Frank Lake were minimal throughout the study, indicating that the typical redox cycling of iron during anoxic conditions was not occurring in Frank Lake's monimolimnion (Figure 1.49, Appendix A). The absence of Fe indicated that it was likely contained in the sediments as FeS (Davison and Heaney 1978). The occurrence of elevated Fe in the Apr 2012, Feb 2013 and May 2013 surface samples was discussed previously.

Zn demonstrated increases at 0-2 m, 9 m and 17-24 m during fall 2011, which was a very similar to the Zn trend in Lim Lake at the same time. Again, phytoplankton presence in the lake during summer was supported by DO and chl *a* trends indicating that Zn harvested by the phytoplankton may have been released during fall decay. The subsequent decrease towards the end of fall was likely the result of precipitation of the oxidized Zn (Hamilton-Taylor *et al* 1996). Si trends in the epilimnion were also characteristic of phytoplankton growth and decay with Si consumed in the summer and then released again during fall (Mir and Kachroo 1982, Mortimer 1941, Munawar and Munawar 1975). The increased Zn concentration that occurred at depth in fall 2011 can be explained by the elevated Zn concentration measured at the inlet after re-initiation of effluent discharge (discussed earlier) (Figure 1.77, Appendix A).

Warm temperatures in February 2013 were the likely cause of changes to some surface parameters similar to the rain event of May 2013. The brown colouration of the Feb 2013 sample also supported an allochthonous source of inflowing water. The brown colouration was attributed to humic or fulvic acids in the water and metals such as Fe often complex with these organic compounds and are prevented from oxidation as a result (Gensemer and Playle 1999, Hem 1960*a*). It is possible that warm temperatures that occurred in Feb 2013 allowing melt-water from shore to flow under the ice. Frank Lake's current water colour is clear and so the stained water must have been from external input. Recall that a similar sample occurred in Lim Lake.

Effluent and Rain: Combined Effect

The combination of the effluent discharge alterations of fall 2011 and the rain event in spring 2013 forced a divide in water quality and had a dominant effect on the ANOVA results for all of the independent variables (layer, year and season). As discussed, parameters that tended to be highly concentrated in the effluent were diluted by the rain while parameters low in the effluent tended to be more concentrated in the natural inputs. It was these parameters that demonstrated a significant level of variability between years (chl *a*, sp-cond, TKN, ammonia, NO3, TDS, Al, Ba, K, Mg, Mo, total sulphur, Si and Cl). However, some parameters that were diluted or further concentrated by the rain had enough influence from the 2013 year of discharge to demonstrate a non-significant variability between years. These parameters included alkalinity, Ca, Fe, Mn, Na, Zn, sulphate and hardness. Other parameters that did not vary significantly between years were only measured up to June 2013 (DIC, DOC, TotP) or were not appreciably changed by the effluent alterations or the rain event (Sr, pH).

Lim Lake and Frank Lake – Other Water Quality Trends

Temperature

Temperature trends in Lim Lake (Figure 1.10, Appendix A) and Frank Lake's (Figure 1.37, Appendix A) mixolimnion were typical of a freshwater lake at this latitude. Solar heating during summer formed thermal stratification while the cooling air temperatures in the fall formed isothermal conditions, allowing the lake to turnover to a depth free from chemical stability.

The meromictic state of Frank Lake slightly altered its seasonal temperature trends. Throughout all seasons, the monimolimnion had a fairly stable and warmer temperature, between 4.4-5°C, compared to the overlying hypolimnion. This increase in temperature in the monimolimnion commonly occurs in meromictic lakes, such as in Soap Lake, WA (Anderson 1958) and Sunfish Lake, ON (Duthie and Carter 1970), and is known as dichothermy, which is thermal stratification with a minimum occurring in the middle lake strata (Hutchinson 1957, Yoshimura 1936*a*, *b*, Yoshimura 1937). Dichothermy occurs in meromictic lakes during summer because surface heating, cooling and wind do not greatly influence the sheltered monimolimnion; therefore allowing it to maintain a more consistent temperature (Yoshimura 1936*a*, *b*, Yoshimura 1937). Any heat gained from sediment or solar radiation that is able to penetrate through the mixolimnion is preserved in the monimolimnion. During late fall, mesothermy occurs in Frank Lake, where a maximum temperature occurs in the middle lake layers, in this case at the chemocline, and this again is commonly observed in meromictic lakes (Hutchinson 1957, Yoshimura 1936*a*, *b*, Yoshimura 1937).

Dissolved Oxygen and Chlorophyll *a*

As mentioned, DO was the best demonstrated turnover extent in both study lakes. The decrease in DO in Lim Lake (Figure 1.11, Appendix A) during summer and winter months could be attributed to animal and plant respiration, bacterial decomposition of organic matter and oxidation of inorganic constituents (Hutchinson 1957). This oxygen depletion can be very detrimental for aquatic organisms; however, much of Lim Lake's volume remained relatively well oxygenated despite these DO depletion events and DO was replenished to the water column during turnover. In Frank Lake, the anoxic conditions present in bottom strata (Figure 1.38, Appendix A) were due to the meromictic state of the lake and the inability of turnover to replenish DO during either spring or fall.

Heterograde DO trends observed in Lim and Frank Lakes could be loosely attributed to phytoplankton photosynthesis and/or zooplankton respiration in the lake. The positive heterograde curve in July 2011 in Lim Lake (Figure 1.11, Appendix A) corresponded with the maximum chl *a* concentration in the water column (Figure 1.12, Appendix A). Correlation of these two parameters has been long observed by limnologists (Eggleton 1956). The heterograde trends of July 2011, April 2013 and August 2013 in Frank Lake (Figure 1.38, Appendix A) were difficult to classify as either negative or positive. By definition the trends were negative, since a metalimnetic minimum concentration occurred (Shapiro 1960, Wetzel 2001). The live *Daphnia sp.* and *Chaborus flavicans* specimens were observed in some of Frank Lake's near-surface and a single chemocline sample respectively, including under the ice, and therefore, respiration and grazing on phytoplankton populations was occurring. This supports the idea of the curves being negative heterograde. In support of these trends being positive heterograde, chl *a* trends demonstrated that there was at least some phytoplankton growth/photosynthesis in the mixolimnion in select strata (Figure 1.39, Appendix A). DO production by phytoplankton populations could have been occurring but populations may not have been high enough to raise DO concentrations higher than at the surface, hence the absence of a DO maximum at these depths.

Without biomass data to support them, using chl *a* concentrations to discuss viable phytoplankton activity is limited but still acceptable. Phaeophytin *a* (chl *a* minus central Mg^{2+} ion) and chl *a* from degrading and settling phytoplankton can be measured by both multi-probe sensors as well as lab extraction methods and can contribute erroneously to the total chl *a* concentration (Cullen 1982, Lorenzen 1965, Lorenzen 1966, Osmund *et al* 1965). Another reason chl *a* data interpretation is limited is due to the fact that phytoplankton populations at depth have been observed to produce higher concentrations of chl *a* due to low light conditions as an adaptive strategy (Cullen 1982) and in such scenarios, chl *a* does not accurately represent biomass.

Despite these potential error sources, the heterograde oxygen trends observed during the study as well as some of the micronutrient trends to be discussed above are all suggestive of the occurrence of at least some phytoplankton/zooplankton dynamics in both lakes. Following the rain event of May 2013, chl *a* increases in Frank Lake surface strata could have been due to phytoplankton growth stimulated by a lower-salinity environment or it could have been allochthonous input of chl *a* from run-off. In general, chl *a* values in Lim Lake and Frank Lake (0.3-3.0 µg L^{-1}) were indicative of oligo/mesotrophic classification (Wetzel 2001).

Specific Conductance and Sulphur Compound Characterization

A double chemocline was observed in Frank Lake during the spring and summer (Figure 1.66, Appendix A). The development and persistence of the upper chemocline, which disappeared during each fall turnover, was a result of both settling of TDS into the hypolimnion and monimolimnion and dilute water loadings from run-off and rain into the epilimnion. The lower chemocline, which was stable throughout the study, was the separation of the mixolimnion and monimolimnion. The shallow chemocline of spring and summer 2013 and shallow turnover to only 6m in fall 2013 were likely a result of the May 2013 rain event and the surface water dilution that ensued. The major rain event and early cessation of effluent discharge in Sept 2012 were the main contributors to sp-cond decrease throughout the study.

The total sulphate to sulphur ratio was typically around 1 during the study identifying that sulphate was the dominant form of sulphur in the water samples (Figure 1.63, Appendix A). Points in time when the ratio was <1, such as in fall 2011 and at the surface in May 2013, indicated that other forms of sulphur were present in the lake, such as H_2S (not sampled in 2011) or organic-S. Organic-S from watershed run-off and wetland inputs could have been the reason for the especially low ratio in May 2013. Although not tested in all sample sessions, no H_2S was detected in samples obtained from Frank Lake and sulphur smell was not commonly apparent in samples. The abundance of sulphur and anoxic conditions in the water column suggest that sulphur reduction forming both sulphides and organic sulphur are occurring in Frank Lake (Carignan and Tessier 1988, Giblin *et al* 1990, Kling *et* al 1991, Rudd *et al* 1986, Nriagu and Soon 1985) and working to reduce concentrations in the water column. Annual inputs from mine effluent were constantly replenishing the lake with sulphate making this mechanism difficult to discern using the sulphur data. The decrease in sulphate during the winter months was likely due to sulphate reduction and allocation to the sediment and the lack of effluent discharge during this time made this mechanism possible to discern (Figure 1.72, Appendix A).

Spangle Lake (Reference Lake)

Spangle Lake demonstrated much lower levels of all parameters than both Lim and Frank Lakes. The fact that this lake had not had any influence from effluent discharge was clearly demonstrated by its water quality. The constant sp-cond from the surface to the bottom of Spangle Lake (Figure 1.79, Appendix A), even during the strongest times of thermal stratification in summer and winter (Figure 1.79, Appendix A), indicated that the lake has not chemical stability influencing its mixing regime. The oxygen depletion at depth in Spangle Lake (Figure 1.78, Appendix A) was not due to incomplete turnovers but rather due to bacterial consumption during decay of organic matter and respiration by zooplankton and fish. The spike in chl *a* at 2 m indicated that some phytoplankton activity also was present in Spangle Lake (Figure 1.78, Appendix A).

Conclusion

Using the water quality data observed in Lim and Frank Lakes through the year as well as at turnover, it is clear that a majority of the differences between the lakes are due to the lakes being in differing stages of meromixis. Recovery of the two lakes to normal conditions will certainly vary and TDS was the best parameter for indicating chemical stability. In Lim Lake, the TDS-contributing parameters decreased markedly during the study. This decrease was accompanied by turnover ability during fall and partially ability during spring in the lake for the first time since the first observation of meromictic conditions in 2008. This monomictic mixing regime removed anoxic conditions during turnover events, which was a great influence on the water chemistry observed in Lim Lake. The management strategy of ceasing discharge in Lim Lake and allowing natural remediation to occur was what allowed the meromictic event in Lim Lake to occur. Although the lake demonstrated great improvement in water quality and mixing ability, the incompleteness of spring turnover in the lake and the presence of elevated concentrations of most parameters indicated that it is still in the process of remediation and both dilution and allocation of sulphate to the sediments during periodic anoxic conditions will be the prime mechanisms by which Lim Lake's remediation continues.

In Frank Lake, the largest influences on the lake's water quality were its continued effluent discharge inputs and stable chemical stability (meromixis). The presence of anoxic conditions year-round in Frank Lake influenced the water quality and the form of chemical species in the lake. Dilution by rain and meltwater as well as high TDS inputs from effluent discharge will continue to control mixolimnion turnover depth during spring and fall in Frank Lake. Similar to Lim Lake, sulphate removal from the water column and allocation to the sediments during anoxic conditions will ultimately reduce TDS in Frank Lake as well. After the cessation of mining, Frank Lake will be included in the post-closure management strategy for the site. At mine closure, elevated levels of TDS from sulphate, Ca, Na, K etc. will still influence chemical stability in the lake. It is likely that both the greater depth and complex bathymetry (bays) of Frank Lake will lengthen the time it takes for it to become free of meromixis compared to Lim Lake. The fact that effluent will continue to be discharged into Frank Lake long after mine closure will influence the lake's recovery. Elevated-TDS effluent will continue to be input into the lake however, the expected lowering of TDS levels in this effluent may help to begin dilution in Frank Lake and slowly deteriorate chemical stability, along with continued inputs from rain and meltwater. This management strategy is different from Lim Lake's and could minimize the potential for the development of a very low TDS upper stratum in Frank Lake.

In addition, it would be interesting to see how the biological components of the lakes change as the meromictic state changes. As dissolved solids in the lakes begin to decrease and turnover becomes exclusively dimictic, habitat area will expand for fish and changes in water and sediment chemistry will follow. Freshwater species that may have been lost from the lake systems due to effluent effects and meromixis may be able to recover in time.

Based on the water chemistry trends in Frank Lake in relation to effluent and precipitation events and the variability in turnover depth from year to year, the exact remediation progression of Frank Lake through post-management strategies and natural remediation is difficult to predict. Remediation is clearly influenced by many variables and required a more detailed study encompassing the dominant variables influencing the water quality in the lake. Utilization of the CE-QUAL-W2 model in Chapter 2 allowed for probable predictions regarding the lake's response to varied TDS inputs and remediation of meromixis in the lake.

CHAPTER 2 – Water Quality Modeling of Mixing Trends in Frank Lake

Introduction

The purpose of studying and/or modeling mine-impacted pits/lakes is often based around the need to maintain meromictic conditions for the purpose of isolating low-quality water, tailings or waste rock from upper strata such that downstream watersheds are minimally impacted (Brassard *et al* 1996, Fisher and Lawrence 2006, Hamblin *et al* 1999, Herrell *et al* 2015, Fisher and Lawrence 2006, Hamblin *et al* 1999, Vandenberg *et al* 2015). A less common but very useful application, which was utilized in the Alberta oil sands, is to model hypothetical systems with differing management strategies in order to determine the potential of meromixis with the goal of preventing meromixis altogether (Mackenzie *et al* 2004). The purpose of the current study was unique in comparison to these other modeling projects since removal of meromictic stability in Frank Lake was the ultimate goal.

As Chapter 1 showed for Lim Lake, after effluent discharge ceased, the TDS of Lim Lake's surface strata quickly declined and initially, meromictic stability developed. Although the meromictic stability in Lim Lake is now deteriorating, the occurrence of meromixis during natural remediation indicated that the current meromictic stability in Frank Lake has the potential to be strengthened and prolonged after its effluent discharge ceases. A water quality model was required to characterize the dominant mechanisms affecting its TDS concentrations and ultimately, its meromictic state. The methodology selected for this purpose was the CE-QUAL-W2 model.

CE-QUAL-W2 Model - Overview

Thomas M. Cole of the United States Army Corps of Engineers and Dr. Scott A. Wells of Portland State University's Environmental and Civil Engineering Department have been the prominent developers of CE-QUAL-W2 hydrodynamic and water quality model since 1975. CE-QUAL-W2 is a two-dimensional, laterally averaged model that can model variables in the longitudinal/horizontal and vertical directions/planes (Cole and Wells 2013). It is well suited to Frank Lake because of the horizontal and vertical variability within the lake. The hydrodynamic portion of the model simulates and predicts water surface elevation, velocity and temperatures. The results of the hydrodynamics equations are coupled to the water quality equations and used to drive the transport of water quality constituents through the system (Cole and Wells 2013). TDS is the proxy for all chemical parameters in the lake (Chapter 1) and will be used in the model to predict the meromictic trends in Frank Lake.

Lowered TDS levels within Frank Lake will begin to occur after effluent discharge water quality improves post-closure and after effluent discharge ceases entirely since the effluent is the source of the higher TDS levels within the lake. The gradual TDS reduction strategies will more effectively breakdown meromictic conditions in Frank Lake since the mixolimnion will not be allowed to rapidly develop a lowered TDS as in Lim Lake. It is hypothesized that having a mixolimnion that is slowly diluted will allow it to mix more effectively with the upper strata of the monimolimnion during turnover events and cause lowering of chemocline stability. It should be noted that once discharge into the lake ceases completely, meromictic conditions could re-initiate and allow meromictic stability to return.

Objectives

1) To collect required field data for the calibration/validation of the CE-QUAL-W2 water quality model to predict TDS concentrations in Frank Lake.
2) After calibration of the model, perform predictive model scenarios that vary TDS input into Frank Lake (10%, 25%, 50% and 75% TDS reductions) to better understand how the meromictic stability of the lake will change in each scenario.

Methods

The field season of 2013 was designed to collect appropriate data for the CE-QUAL-W2 model and build its required input files to simulate temperature and TDS. A much more detailed description of model set-up can be found in Appendix C. The model is developed in four steps: 1) bathymetry and topographic datasets are used to build the model grid, 2) input files for boundary conditions, initial conditions and model control are built, 3) model calibration/validation is performed by comparing model outputs with observed calibration data, and 4) the model is used to make predictions representative of user-devised scenarios.

Bathymetry, Topography and Model Grid Development

This comprises the geometric data requirements of the model. Bathymetric data from within the lake was obtained using a depth sonar and UnderSee Explorer software. The final data set was composed of latitude, longitude and depth (x, y and z) data points. Topographic data was obtained from the geogratis government website and was merged with the bathymetric data set in Golden Software's SURFER 12 program. The final map and boat passes are displayed in Figure 2.1. Development of the model grid also occurred in SURFER using the thalweg and shoreline morphometry to build the segments and an automated script to iteratively develop the layers within each segment (Figure 2.2). Segment lengths were kept relatively consistent to ensure numerical stability of the model. Shoreline morphometry is what dictated segment size and orientation. When the lake width from shoreline to shoreline changed appreciably, a new segment was used to represent that area of the lake. Figure 2.3 conveys the branches and segments developed for Frank Lake. Ultimately, a 3-branch grid was formed with 52 segments and 33 layers. An internal head boundary was used to connect branch 2 and branch 3 with branch 1 at segments 4 and 13 respectively and ultimately forming the bathymetry file.

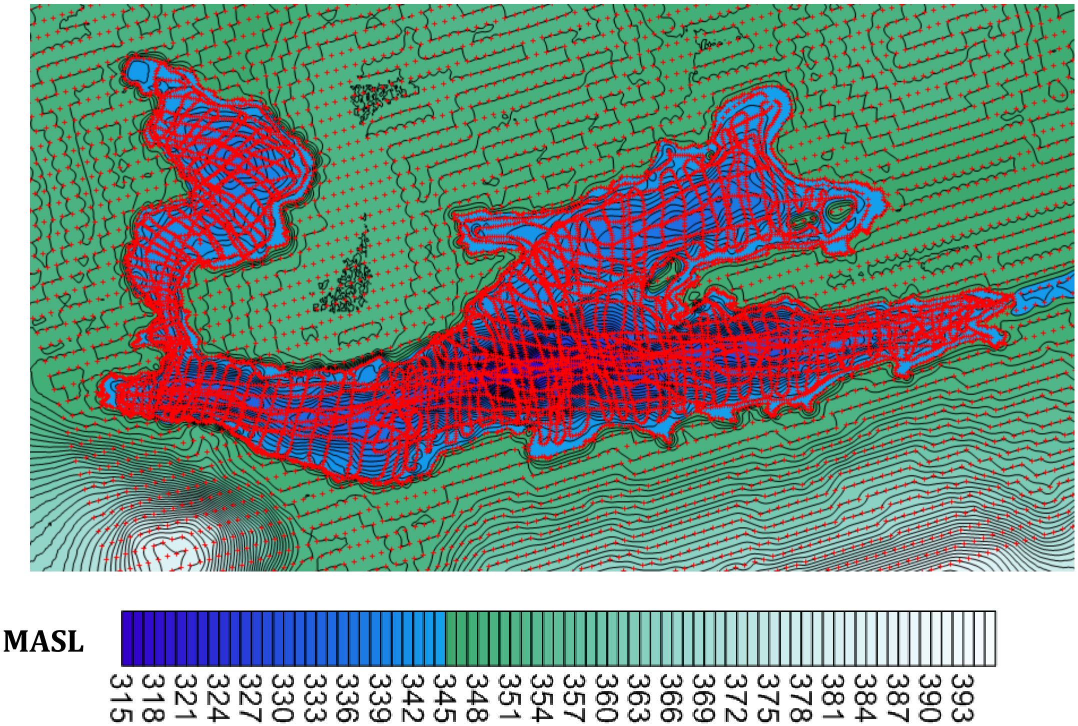


Figure 2.1. Frank Lake boat tracks for collecting bathymetry dataset. The merged DEM points are also shown for the topography and MASL elevations.

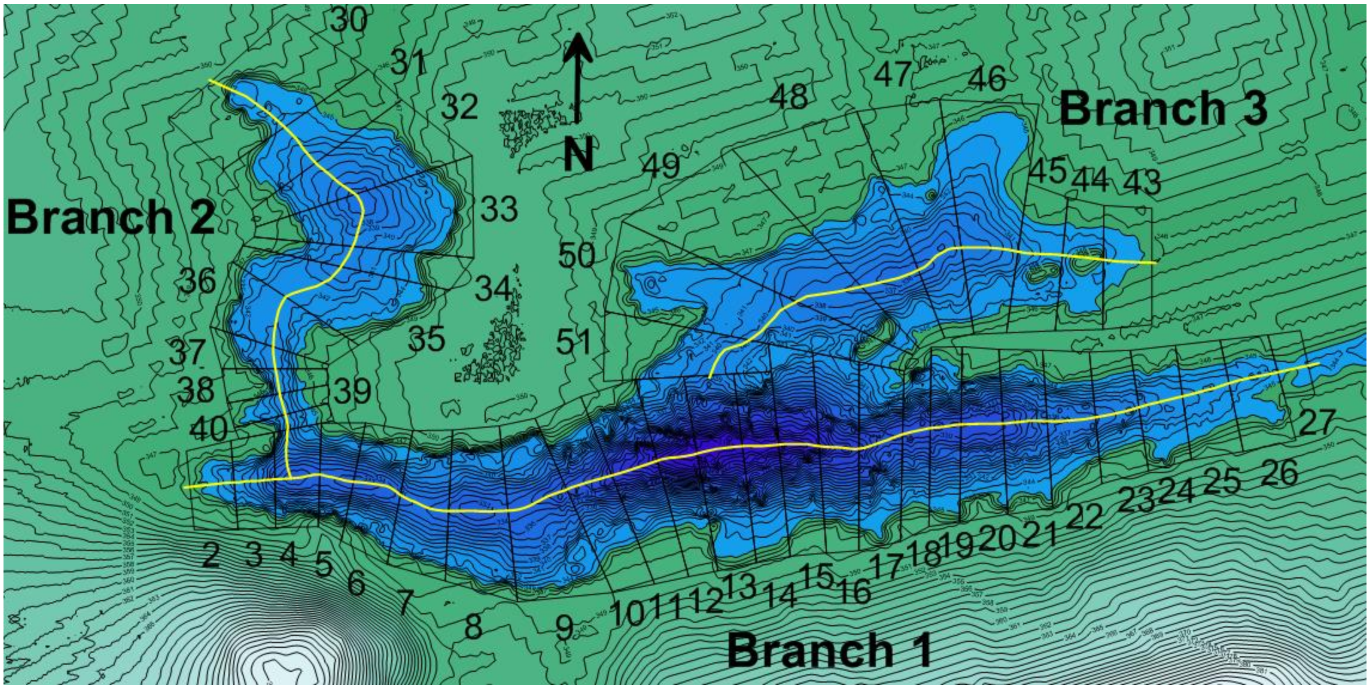


Figure 2.2. Frank Lake thalwegs used for segment placement ultimately used for model grid development.

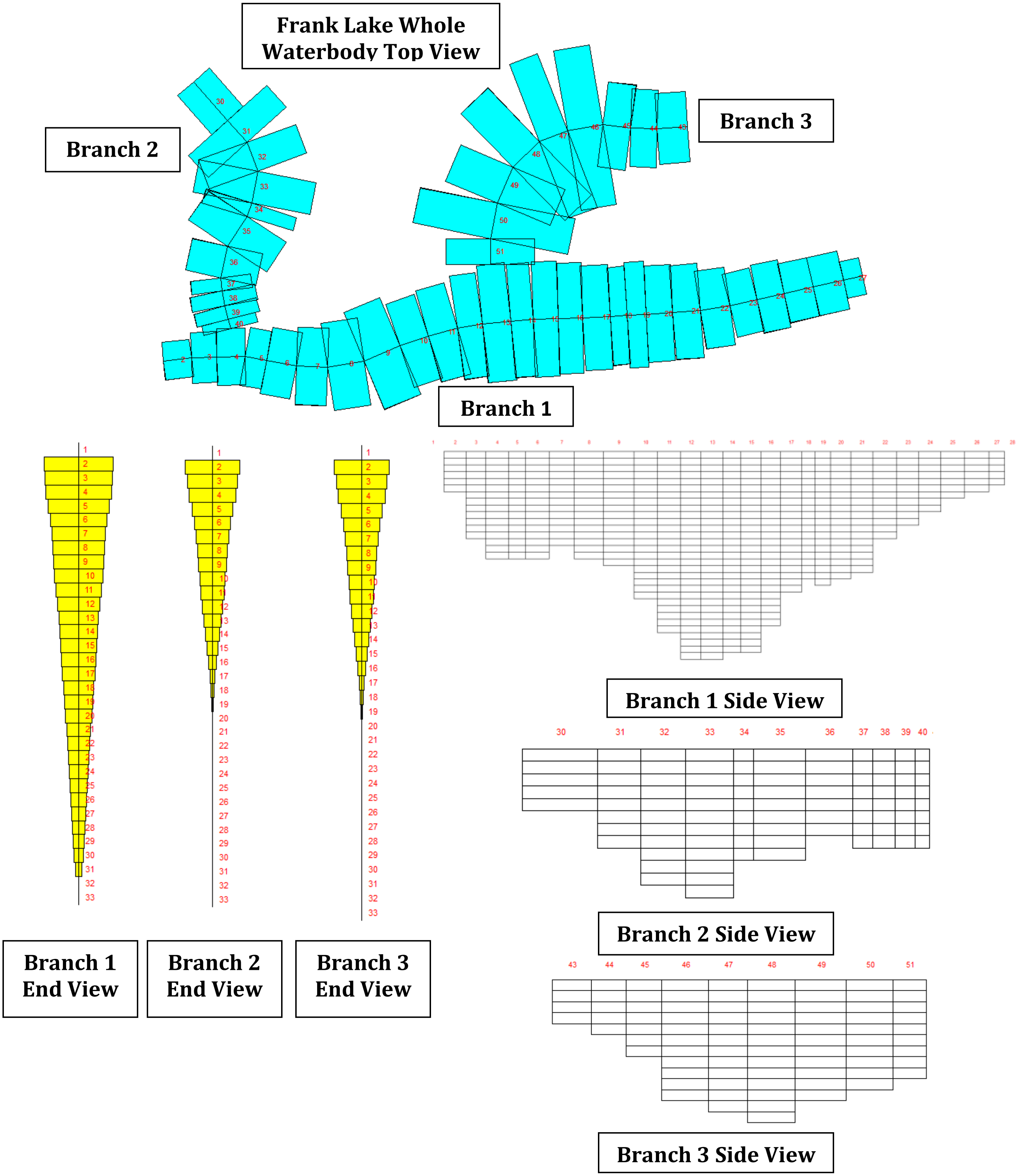


Figure 2.3. W2 Control and Bathymetry GUI projections of the top, side and end views of the Frank Lake model grid.

Boundary Condition Data

Flow rate (ft sec^{-1}) data was collected during each sample session at the inlet and outlet. For modeling purposes, flow rates were converted to flow volumes (m^3 sec^{-1}) using stream cross-sectional dimensions (Buchanan and Somers 1976).

Temperature and conductivity were measured at the inlet and outlet and pressure was measured within the lake every 30 minutes using data logger instruments. Data logger software was used to convert conductivity to specific conductance and pressure to water elevation. Pressures were also barometrically compensated and double checked using staff gauges in the lake. All of the sp-cond and TDS values measured in the lab were used to develop a correlation and equation such that sp-cond data could be converted to TDS for model input.

Meteorological data was measured hourly at the site station and an input file containing temperature, dew point temperature, wind speed, wind direction, cloud cover and short-wave solar radiation was developed for the model.

Initial Conditions

The initial conditions were organized into a longitudinal profile file, which gave each segment and layer in the model a specified temperature and TDS data value. Data acquired from Frank Lake's deep zone in the main channel were used to create this file and initial all branches in the grid. The model was started on April 11, 2013 at 11:30 am, Julian Day=101.48). An initial ice thickness of 0.4m was used (field measured).

Calibration Data

Data was measured at the deep zone within Frank Lake on April 11, 2013 at 11:30am (initial conditions) (JDAY=101.48), May 22, 2013 at 12:00pm (JDAY=141.50), June 11, 2013 at 12:00pm (JDAY=162.50), August 19, 2013 at 12:00pm (JDAY=162.50) and November 13, 2013 at 12:00pm (JDAY=316.50).

Model Calibration

Using all of the data, input files were built and an in-depth model calibration and sensitivity analysis was performed using the CE-QUAL-W2 version 3.72 software. Initially, model simulations were performed for only flow and temperature to ensure that the heat budget (inflow and outflow temperatures and meteorological data) and associated hydraulic coefficients were adequately captured and appropriate. Including water quality computations in the initial calibrations adds in unnecessary complexity that can convolute the user's analysis of model calibration. Only after confirming that momentum and heat are being properly predicted by the model is it practical to "turn ON" water quality computations in the model and allow it to calculate and predict TDS concentrations. The control file for the model is used to turn "ON" or "OFF" water quality computations. Simply put, the hydrodynamics were calibration/validation was performed first and then the water quality calibration/validation was performed thereafter. Main parameters adjusted during the calibration process for the Frank Lake model are outlined in the results and discussion sections.

Model Simulation Scenarios

Once the model was properly calibrated and encompassed the main mechanisms influencing the transport of momentum, heat and the TDS water quality constituent in Frank Lake had been characterized, short-term predictive simulations were performed. TDS concentration at the lake inflow was the only variable adjusted during the simulations. A summary of the scenario simulations performed was outlined in Table 2.1. The simulations were performed for one year and all other boundary condition data and coefficients were held constant during each simulation. The TDS concentration reductions for the scenarios were selected for the purpose of experimentation to understand the short-term response of the lake over a wide range of TDS input reductions.

Table 2.1. Details of predictive TDS scenarios simulated for Frank Lake.

Scenario Number	TDS Concentration Reduction	Result Figure
1	10%	Figure 2.18
2	25%	Figure 2.19
3	50%	Figure 2.20
4	75%	Figure 2.21

Results

Model Calibration

Model Grid

The volume-elevation comparison from both UnderSee Explorer (field bathymetry data) and SURFER 12 (model grid data) indicated a strong agreement of the volume (m^3) versus elevation (masl) (Figure 2.4). This indicated that lake volume and dimensions were preserved during grid development. The UnderSee volume was 4.0% higher; having an additional 100,000 m^3 more water than the SURFER volume. It was possible that some volume was lost between the segments during the blanking procedure as a result of the interpolation occurring in the gridding algorithms in SURFER.

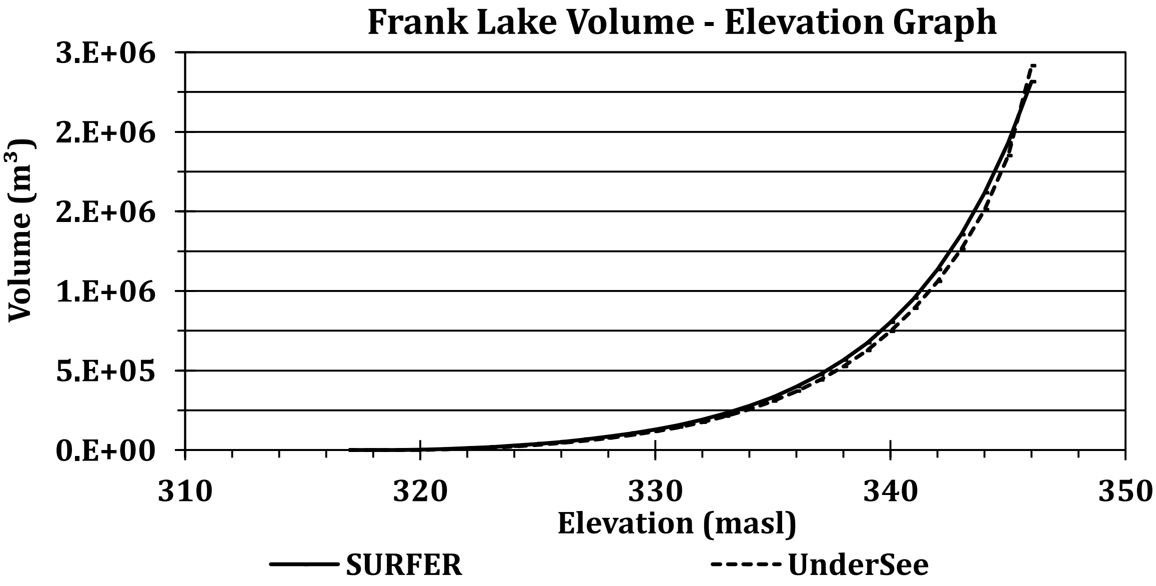


Figure 2.4. Volume-elevation graph for Frank Lake raw bathymetry (UnderSee) and model grid (SURFER) datasets.

Water Balance

Field-measured water elevation from the data logger in Frank Lake and the water level output from the model demonstrated a relatively successful water balance (Figure 2.5), with some deviation occurring early in the year from April to July (Figure 2.6). This confirmed that inflows, outflows and meteorological inputs and outputs were captured relatively well in the field.

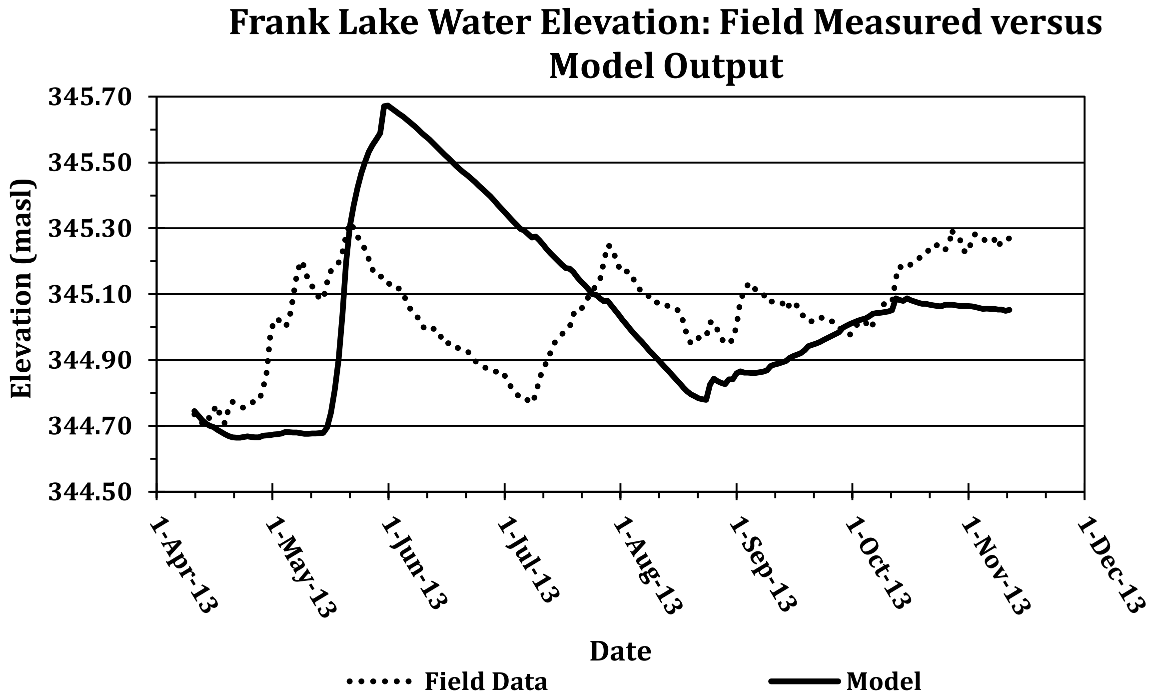


Figure 2.5. Water elevation measured in the field versus elevation predicted by the model.

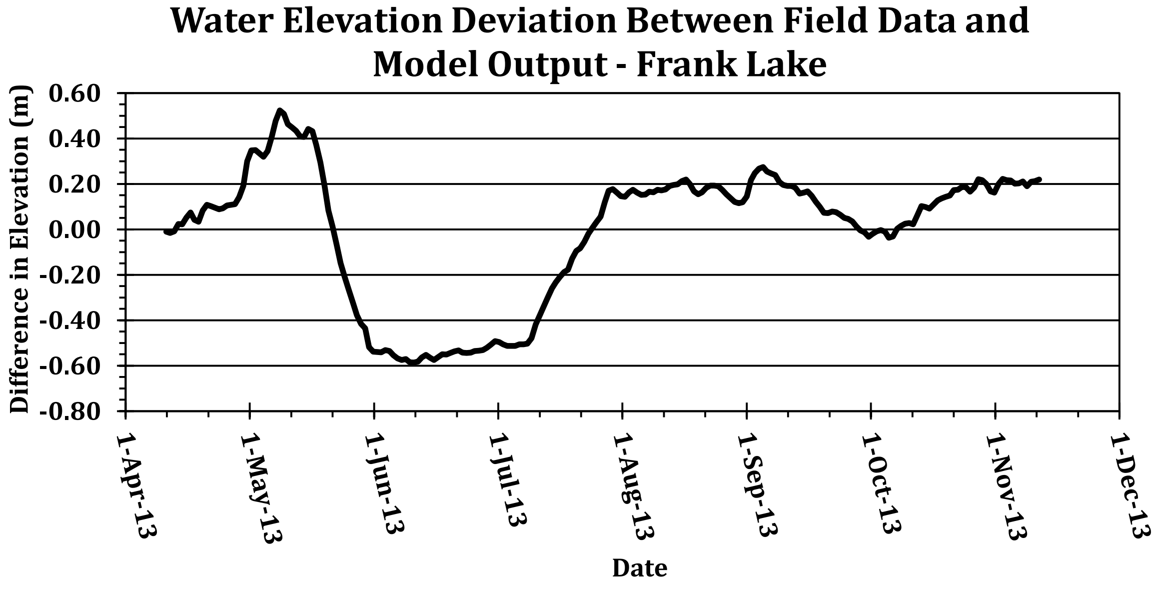


Figure 2.6. Deviation in water elevation measured in the field versus elevation predicted by the model.

Temperature and Total Dissolved Solids

Initially, temperature simulations were performed with water quality computations “turned OFF” in the model to confirm heat budget accuracy. The initial calibration simulations for temperature using the default hydraulic coefficients and recommended settings demonstrated good surface temperature agreement between the model and the field profiles however, the simulated thermocline was deeper than observed (Figure 2.7). In addition, the bottom strata temperatures were warmer than observed. The average mean error (AME) values for four of five of the simulations were all >1.0°C indicating that improvement was required. Field-observed data (calibration data) were physically measured in the lake while the model-predicted data was outputted from the model based on boundary conditions.

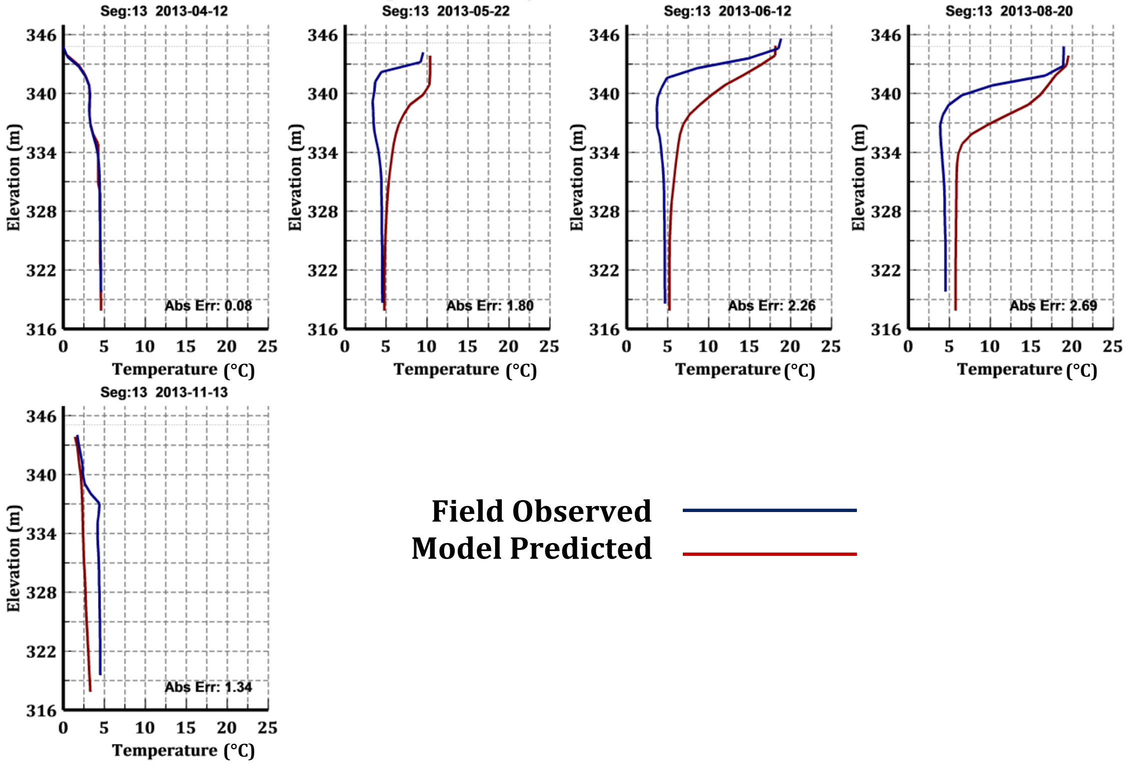


Figure 2.7. Frank Lake 2013 temperature simulation with water quality computations “turned OFF”, default coefficients and recommended settings used.

Adjustment of the wind-sheltering coefficient to reduce the effect of the wind on the lake's surface and decreasing the sediment temperature from 8.0°C to 6.0°C, calibration results improved and the AME's were all <1.0°C excluding November 2013's profile (Figure 2.8).

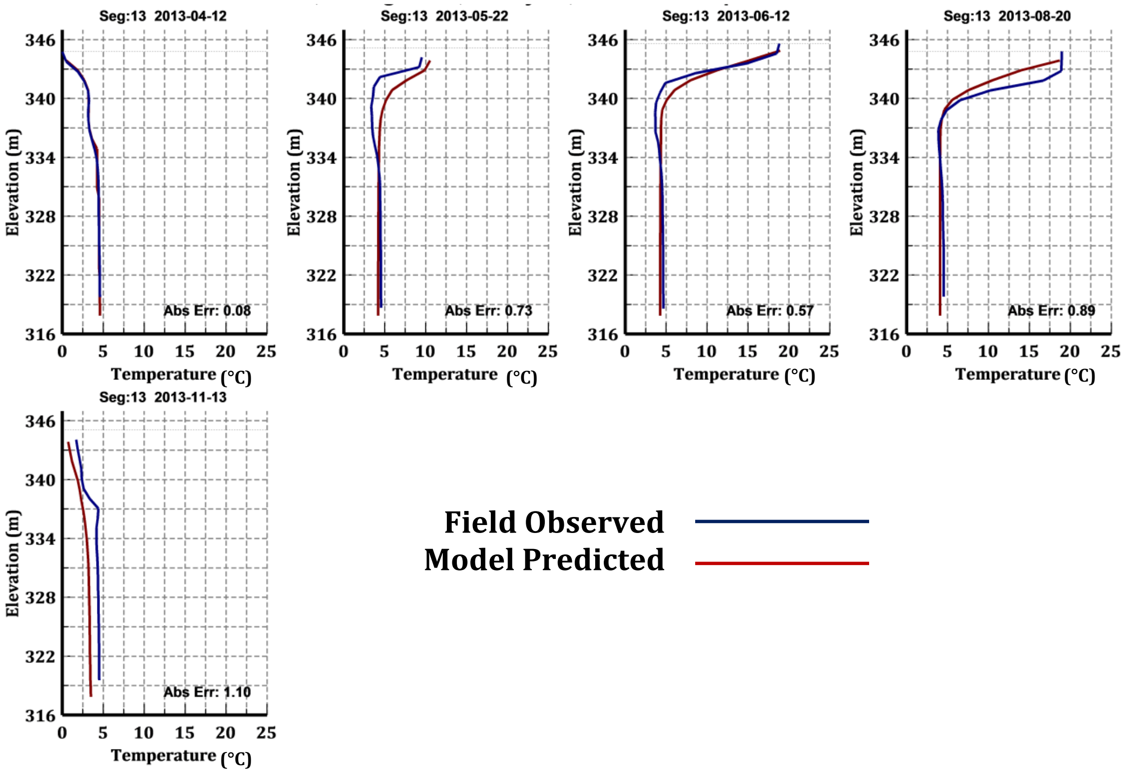


Figure 2.8. Frank Lake 2013 temperature simulation with water quality computations "turned OFF", wind-sheltering coefficient and sediment temperature adjusted.

Following successful heat budget calibration, water quality computations were “turned ON” in the model and the temperature plots were once again analyzed (Figure 2.9). Including TDS simulation into the model negatively impacted the temperature calibration results as indicated by the increased AME’s. Good upper and lower strata temperature simulation occurred but the predicted thermocline was much deeper in the water column than expected. The main observation drawn from this was that TDS was having a substantial influence on momentum and heat transfer within Frank Lake.

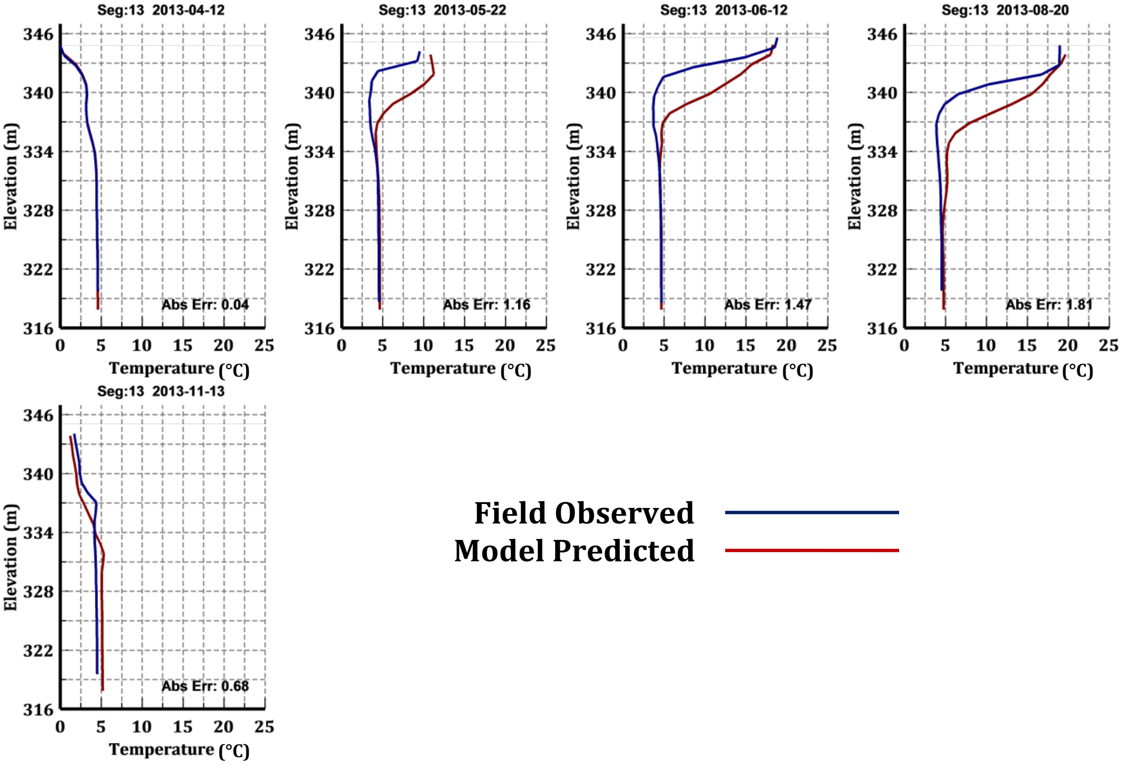


Figure 2.9. Frank Lake 2013 temperature simulation with water quality computations “turned ON”, wind-sheltering coefficient and sediment temperature adjusted same as previous.

With TDS computations now present in the model, TDS simulations were produced. The TDS simulations demonstrated that the model predicted the general trends of the double chemocline in Frank Lake reasonably well, especially in the early part of the year. In addition, the depth of turnover in both April and November

2013 was captured appropriately and the monimolimnion of Frank Lake was maintained throughout the simulation (Figure 2.10).

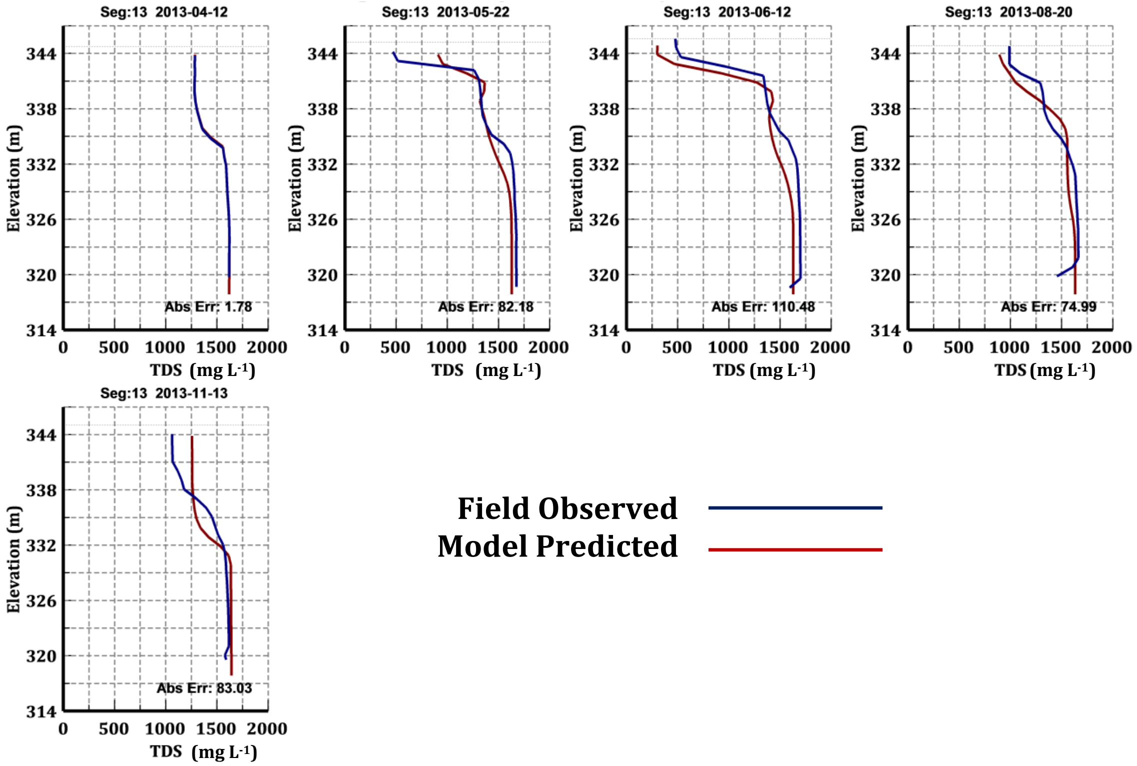


Figure 2.10. Frank Lake 2013 TDS simulation with water quality computations “turned ON”, wind-sheltering coefficient and sediment temperature adjusted.

In order to better understand the effect of TDS on the heat budget in Frank Lake and ultimately improve the temperature simulation with TDS computations now included in the model (Figure 2.10), a sensitivity analysis was conducted. This analysis involved adjustment of coefficients that control how solar radiation and heat were being distributed and transported in Frank Lake. A summary of these coefficients and their final adjustments can be found in Table 2.2 in Appendix C. After adjusting these coefficients, the temperature (Figure 2.11) and TDS calibrations (Figure 2.12) greatly improved and lowered AME’s occurred for all calibration dates. The average mean errors for the five calibration dates were 0.04°C, 0.36°C, 0.41°C, 0.95°C and 0.55°C. These indicated on average the difference between the model predicted and field observed data at any given depth.

Respectively, each of these average mean errors were 1.08%, 7.85%, 6.91%, 14.08% and 14.38% of the average temperature observed in their respective plot. The thermocline in Frank Lake was simulated much more accurately and closely matched the observed profile. The chemocline profiles and depths became more refined in the TDS simulations as well. The average mean errors for the five calibration dates were 1.78 mg L^{-1}, 76.62 mg L^{-1}, 94.45 mg L^{-1}, 61.66 mg L^{-1} and 71.76 mg L^{-1}. Respectively, each of these average mean errors were 0.12%, 5.19%, 6.51%, 4.23% and 5.02% of the average temperature observed in their respective plot. This simulation was the best possible calibration obtained for simulating both temperature and TDS in Frank Lake.

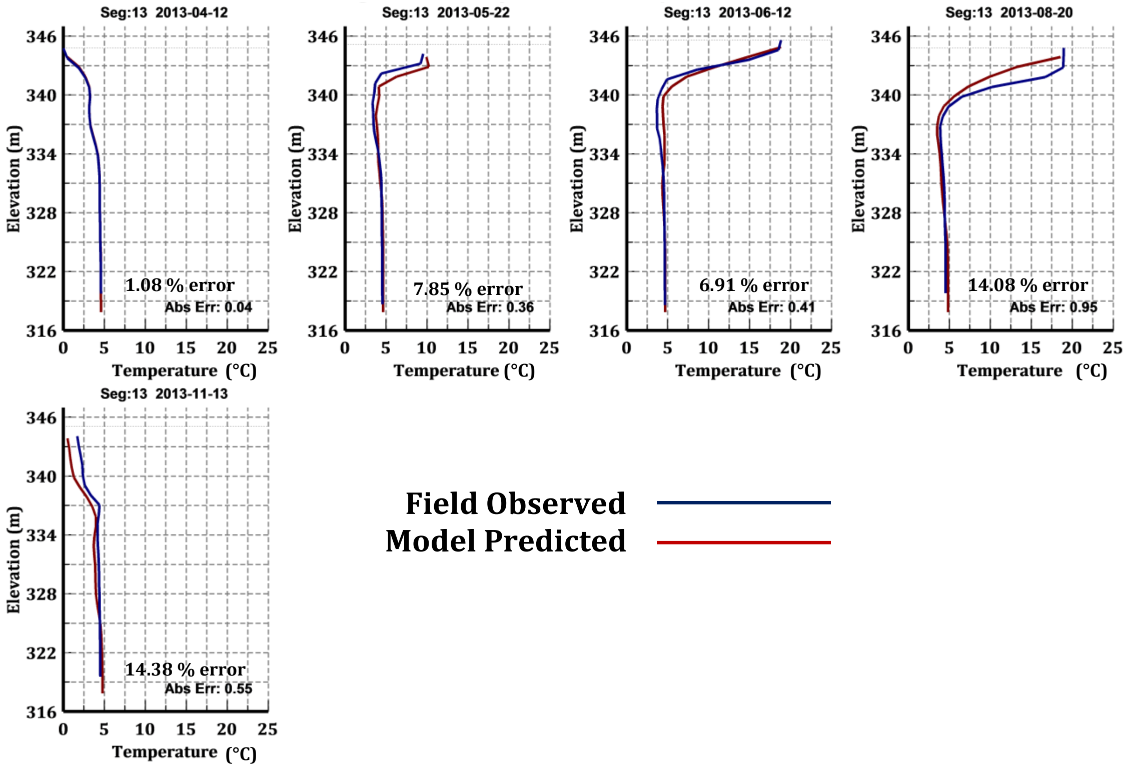


Figure 2.11. Frank Lake 2013 temperature simulation with water quality computations "turned ON", wind-sheltering coefficient, sediment temperature and solar radiation coefficients adjusted.

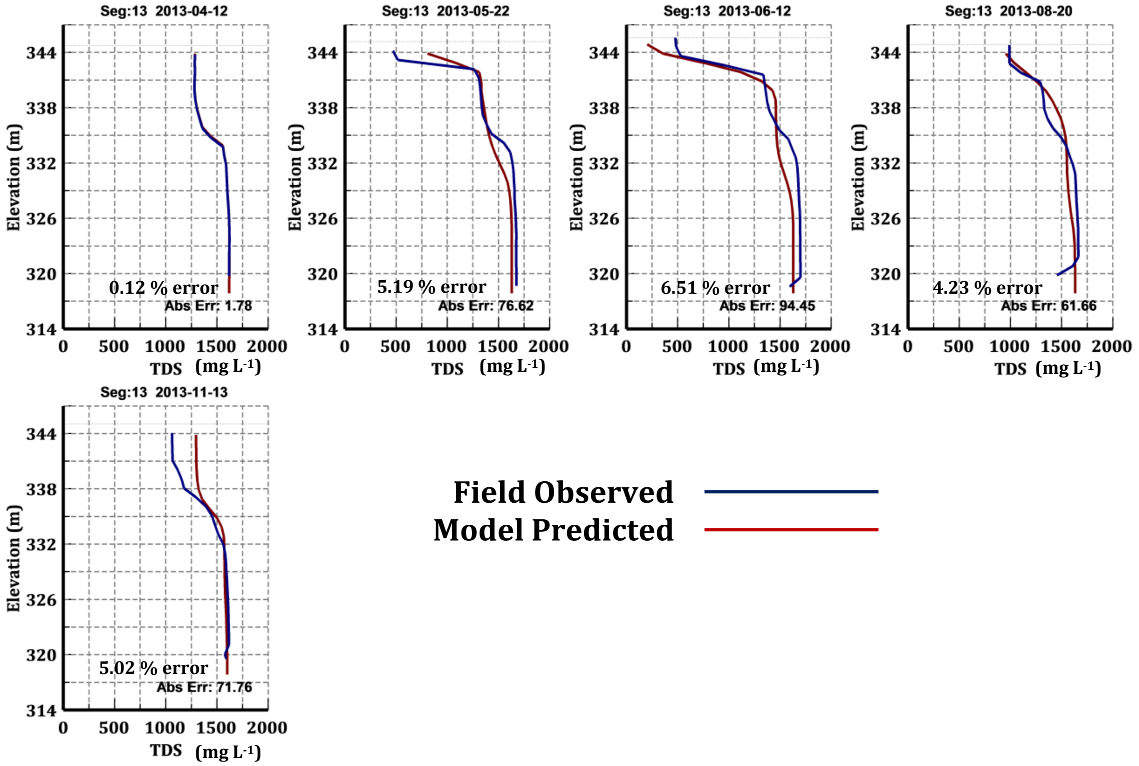
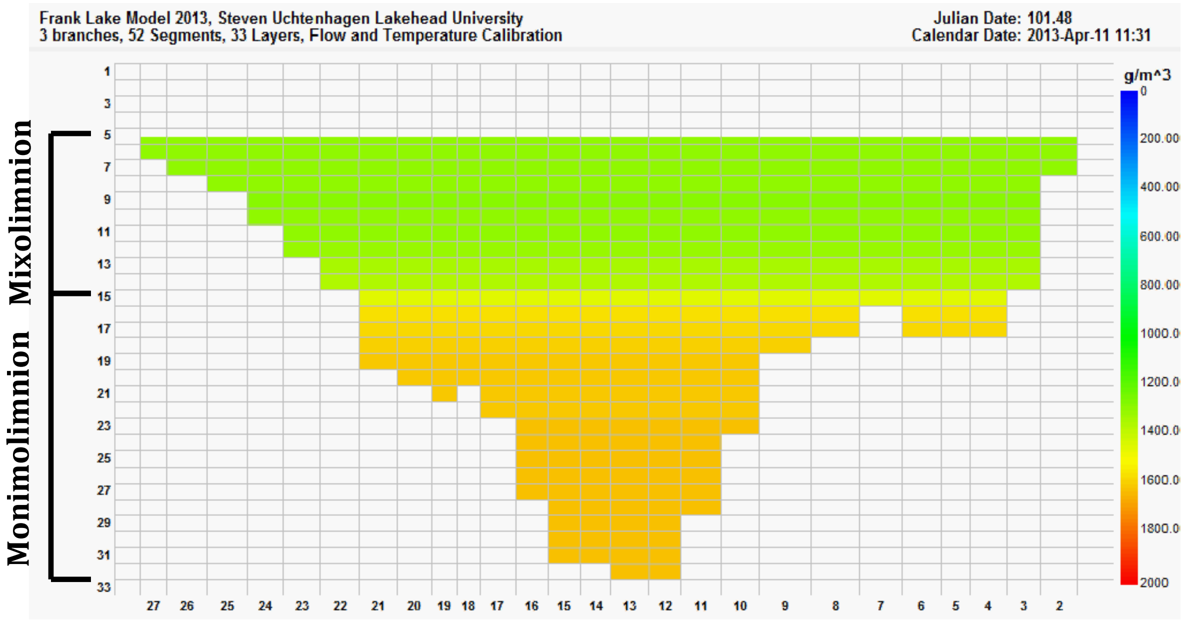


Figure 2.12. Frank Lake 2013 TDS simulation with water quality computations "turned ON", wind-sheltering coefficient, sediment temperature and solar radiation coefficients adjusted.

Model Animations

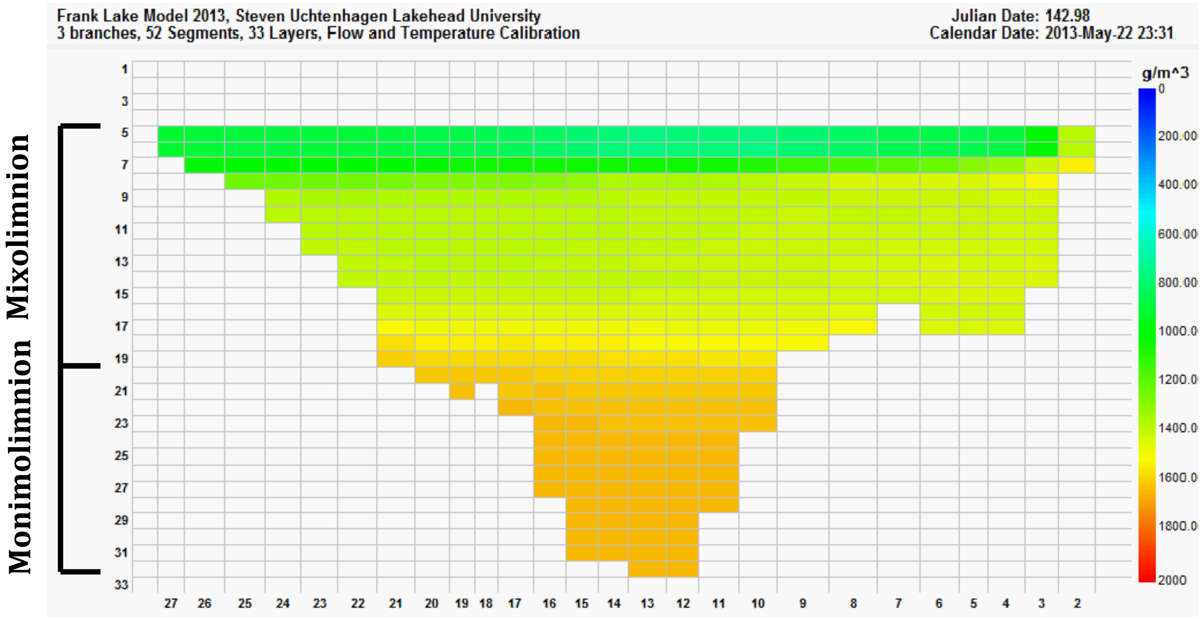
Animations (videos) of the entire 2013 model simulation for temperature and TDS are present on a CD-ROM as Windows Media Player file located at the end of this document. Figures 2.13-2.17 illustrate the grid animations for TDS on the dates that observed/calibration data was measured in the field. Units are in g m^3 which is equivalent to mg L^{-1}. The distinct mixo- and monimolimnions were clear in the model start and end simulations (Figures 2.13 and 2.17 respectively). The rain event and its associated surface dilution were clear in the May and June simulations (Figures 2.15 and 2.15 respectively). The August simulation (Figure 2.16) illustrated the effect of effluent discharge and increased TDS on the surface strata of the lake.



Frank Lake Model 2013, Steven Uchtenhagen Lakehead University
3 branches, 52 Segments, 33 Layers, Flow and Temperature Calibration

Julian Date: 101.48
Calendar Date: 2013-Apr-11 11:31

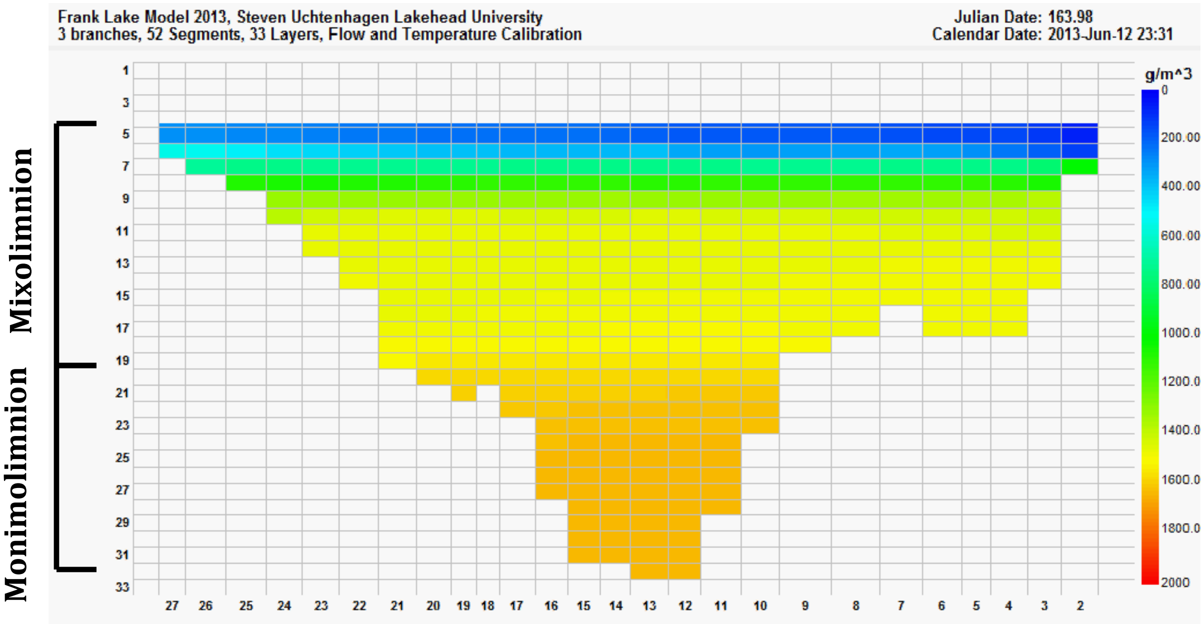
Figure 2.13. Screenshot of Frank Lake 2013 TDS simulation animation on April 11, 2013 (model start).



Frank Lake Model 2013, Steven Uchtenhagen Lakehead University
3 branches, 52 Segments, 33 Layers, Flow and Temperature Calibration

Julian Date: 142.98
Calendar Date: 2013-May-22 23:31

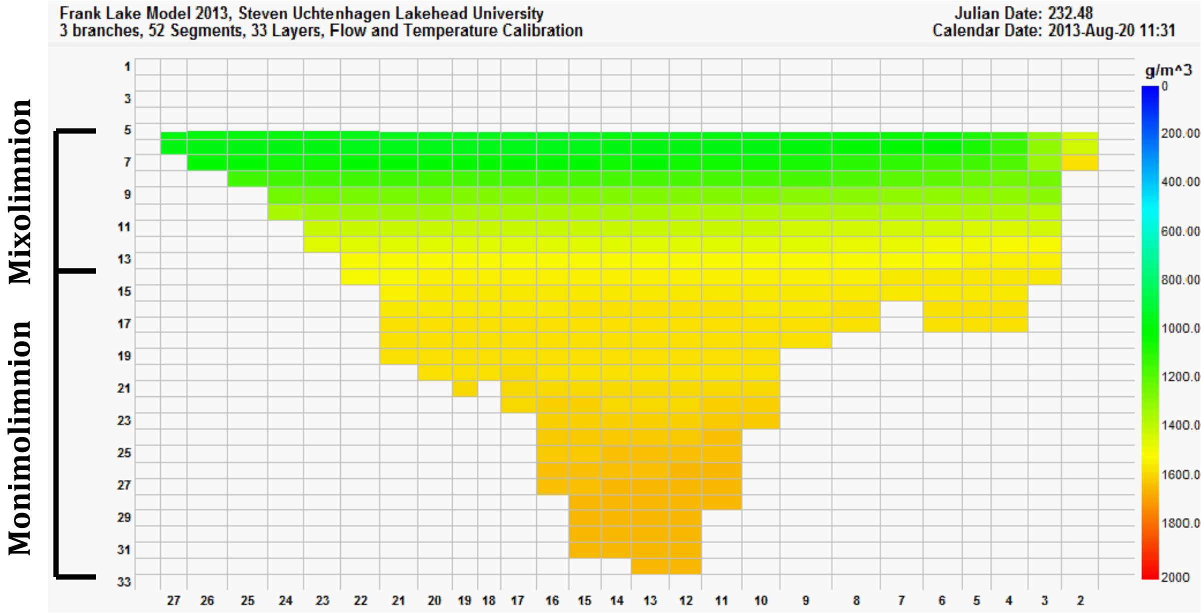
Figure 2.14. Screenshot of Frank Lake 2013 TDS simulation animation on May 22, 2013.



Frank Lake Model 2013, Steven Uchtenhagen Lakehead University
3 branches, 52 Segments, 33 Layers, Flow and Temperature Calibration

Julian Date: 163.98
Calendar Date: 2013-Jun-12 23:31

Figure 2.15. Screenshot of Frank Lake 2013 TDS simulation animation on June 12, 2013.



Frank Lake Model 2013, Steven Uchtenhagen Lakehead University
3 branches, 52 Segments, 33 Layers, Flow and Temperature Calibration

Julian Date: 232.48
Calendar Date: 2013-Aug-20 11:31

Figure 2.16. Screenshot of Frank Lake 2013 TDS simulation animation on August 20, 2013.

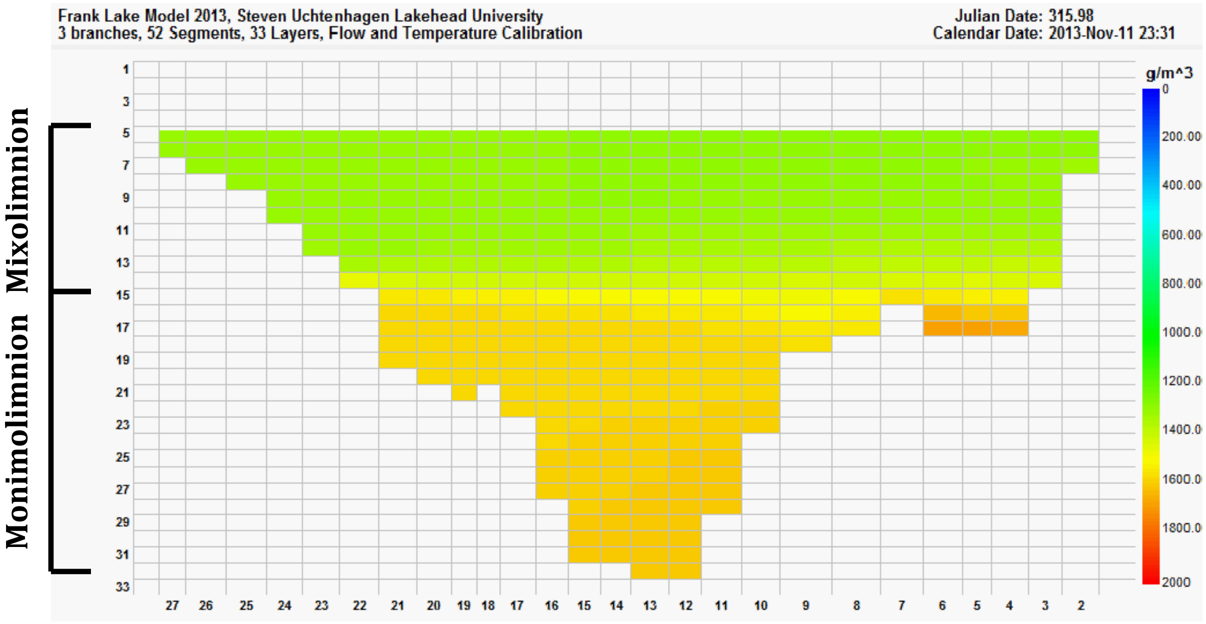


Figure 2.17. Screenshot of Frank Lake 2013 TDS simulation animation on November 13, 2013 (model end).

Model Predictive Simulations

The TDS simulations for Frank Lake for scenarios 1 through 4 are present in Figures 2.18-2.21 respectively. The most notable changes in TDS concentrations occurred near the surface strata of Frank Lake, particularly during August and November. The further the TDS concentrations was reduced, the lower the TDS concentration in the surface strata during August and November. A stable chemocline was maintained in each scenario with some variability in the chemocline depth occurring in the 50% and 75% reduction scenarios. In these scenarios, the chemocline became shallower after fall turnover and a sharper chemocline was observed, indicating an increase in meromictic stability had occurred. Regardless of the scenario tested, the monimolimnion TDS concentration was the same in each and no reduction in monimolimnion TDS was observed.

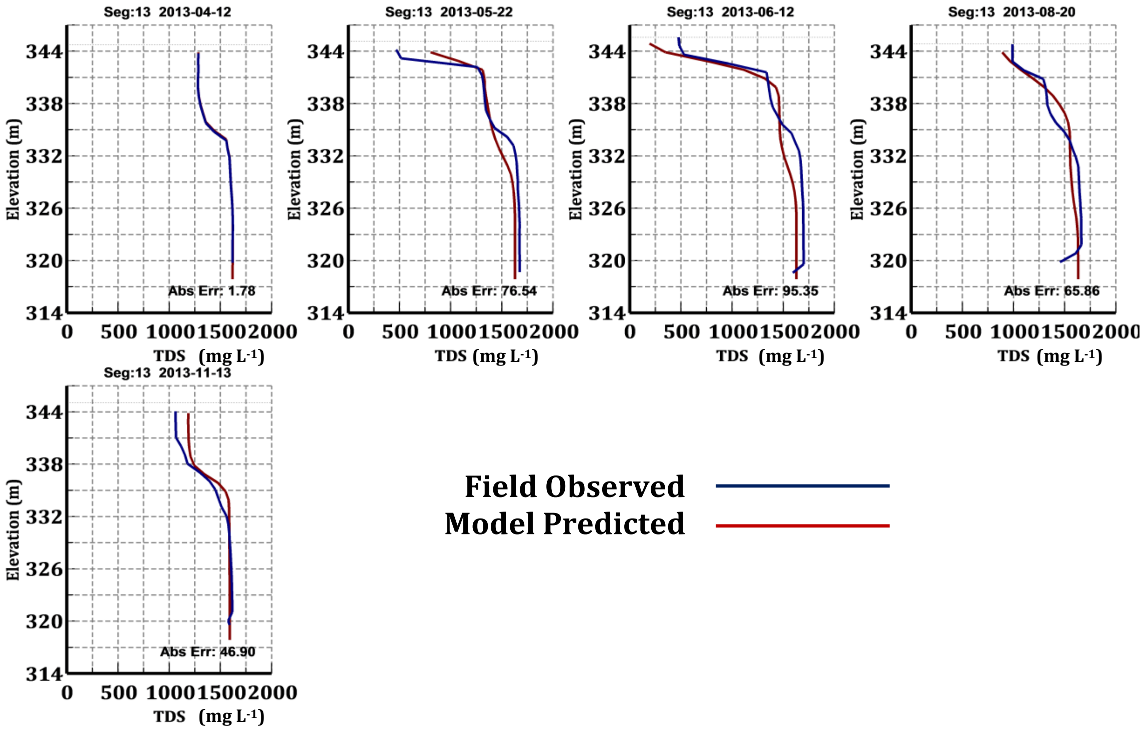


Figure 2.18. Frank Lake 2013 TDS simulation with concentrations reduced by 10%.

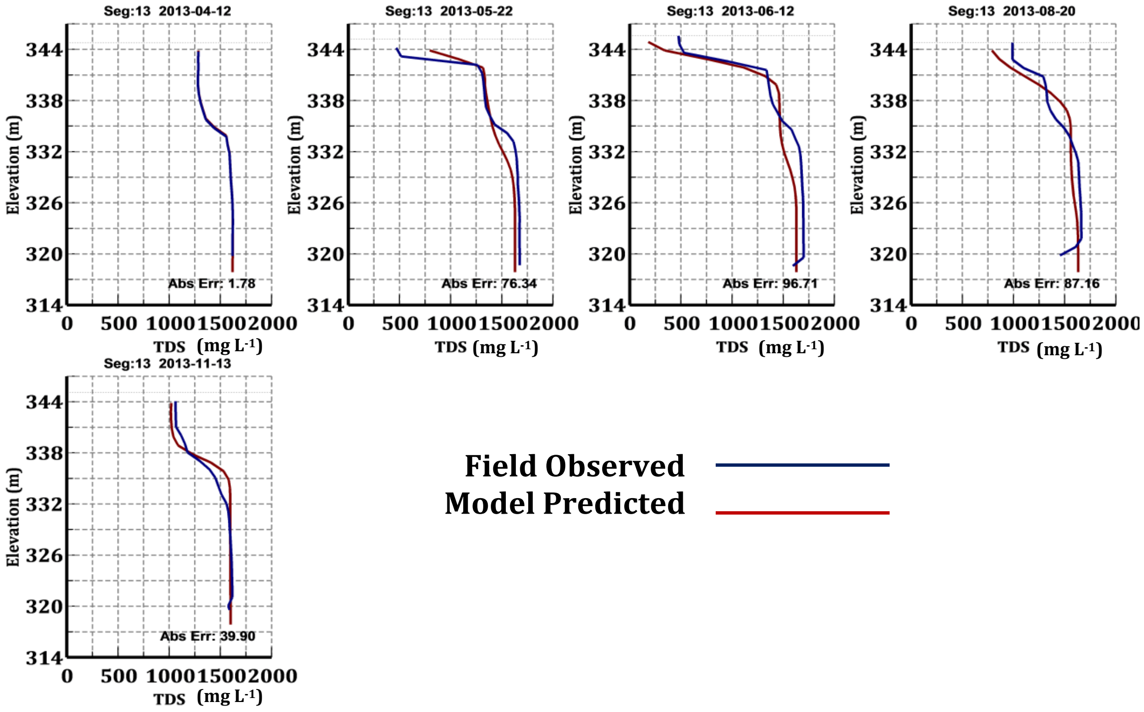


Figure 2.19. Frank Lake 2013 TDS simulation with concentrations reduced by 25%.

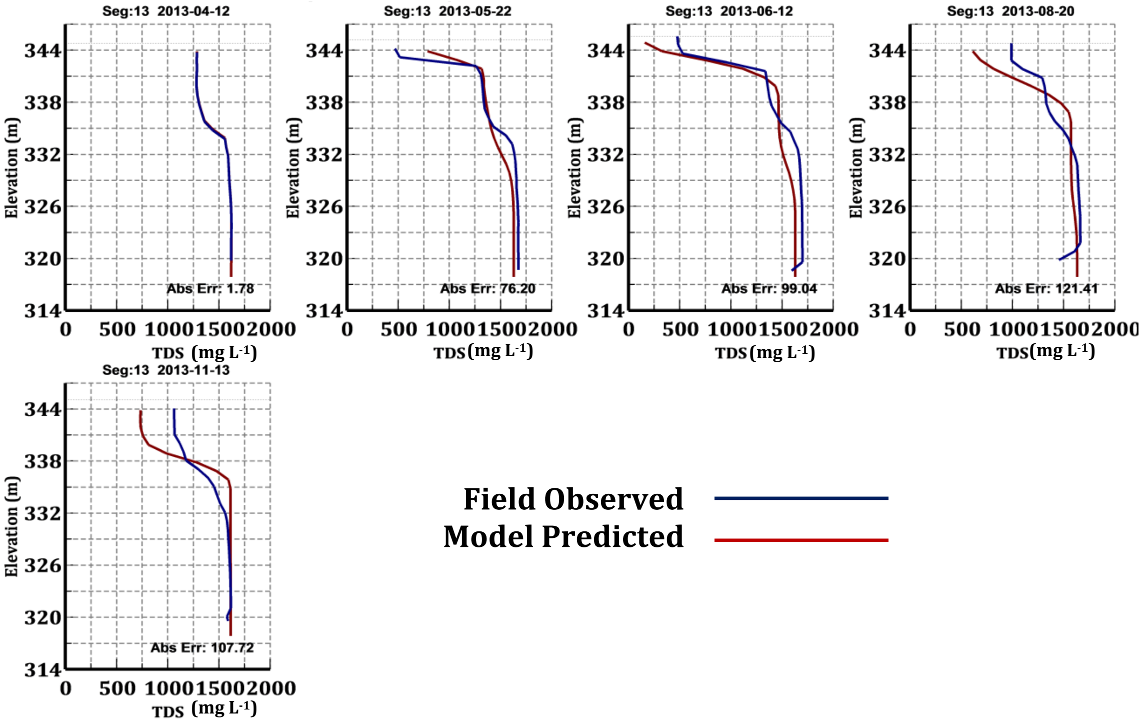


Figure 2.20. Frank Lake 2013 TDS simulation with concentrations reduced by 50%.

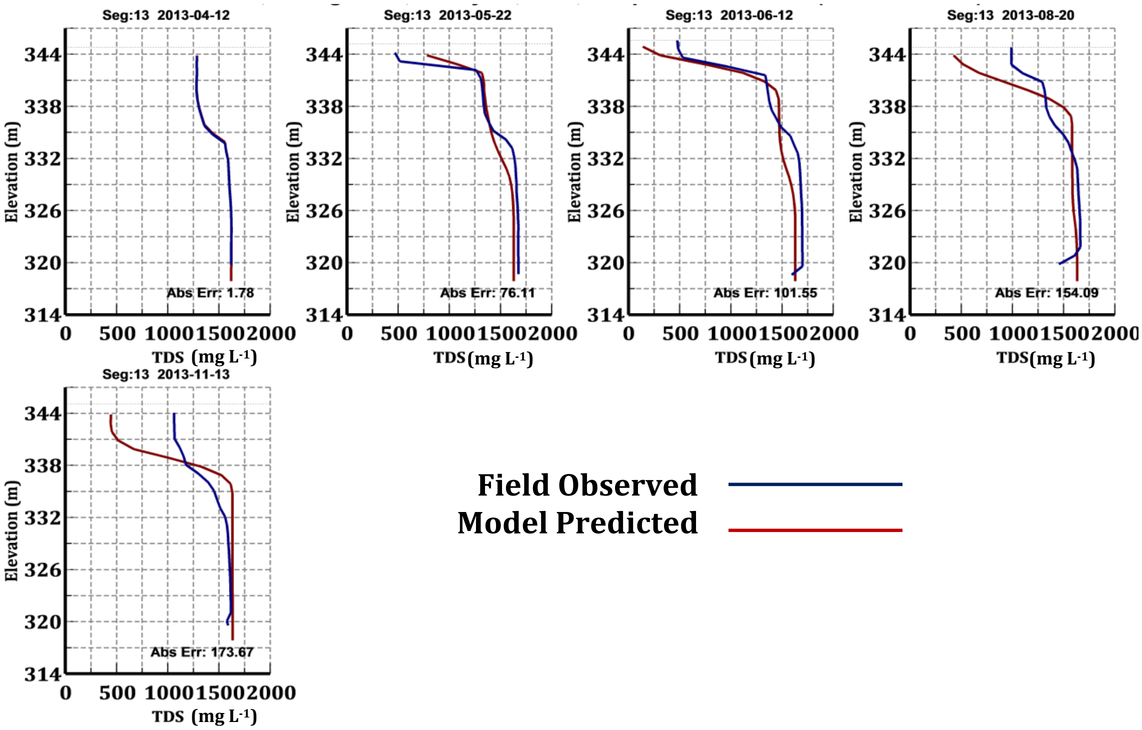


Figure 2.21. Frank Lake 2013 TDS simulation with concentrations reduced by 75%.

Discussion

The main objectives of this chapter were to calibrate the CE-QUAL-W2 model for temperature and TDS and then run TDS reduction scenarios to understand how Frank Lake's meromictic stability would respond.

CE-QUAL-W2 was utilized for this study because it was known that 2D-variability was present within the Frank Lake system due to inflows dispersing horizontally across the lake (high-TDS influent or low-TDS natural inflow). In addition, the model is capable of performing long-term simulations by varying the computational time-step and can effectively model TDS.

Calibration

The calibration process for the Frank Lake model required adjustment of a variety of coefficients to better represent the mechanisms controlling distribution of momentum, heat and TDS concentrations in Frank Lake. A summary of the coefficients adjusted and their final value were listed in Table 2.2 in Appendix C. It is worth briefly discussing these coefficients and their function because they were indicators of mechanisms occurring in Frank Lake during 2013.

To improve the initial temperature calibration (Figure 2.7), the coefficients controlling sediment temperature (TSED) and the magnitude of the effect of the measured wind speeds on the lake surface (wind sheltering coefficient, WSC) were adjusted. Adjustment of the sediment temperature improved model prediction deviations that were occurring in the bottom strata of Frank Lake. An initial value of 8.0°C was used because it was recommended to use the average annual air temperature of the area as the sediment temperature for initial model runs (Cole and Wells 2013). However, this technique is not always an accurate representation of reality and with the persistent 4-5°C water in the monimolimnion of Frank Lake, sediment temperatures are likely not 8.0°C. A value of 6.0°C was used, since sediment in littoral zones above the chemocline will heat during the summer months. The wind-sheltering coefficient was adjusted from the original value 0.7-0.8 down to 0.4-0.5. Essentially what this meant was that all of the wind speeds were reduced by a factor of 0.4-0.5, thus decreasing the amount of surface mixing in

Frank Lake. This reduction in wind effect is a common practice in modeling since meteorological stations are often in non-sheltered areas compared to aquatic systems and are not surrounded by topography and vegetation. For the current study, an improved temperature calibration resulted with wind reduction however, the values used (0.4-0.5) are typical of values used in modeling in mountainous regions with substantial wind-sheltering topography (Cole and Wells 2013). Meteorological data was collected from the top of the tailings area dam and may have been measuring a greater wind speed than what was actually occurring at the surface of Frank Lake. So, it is possible that a coefficient adjustment of such a large magnitude was appropriate.

In order to improve temperature calibration after TDS computations had been included in the model, the fraction of incident solar radiation absorbed on the surface (BETA) and the light extinction coefficient (EXH2O) were adjusted. The BETA coefficient controlled the fraction of incident shortwave solar radiation absorbed on the surface (longwave components of shortwave solar) and it is closely connected with the EXH2O variable (Cole and Wells 2013, Williams *et al* 1980). To achieve an appropriate calibration, a BETA value of 1.0 was required. This ensured that 100% of the longwave incident solar radiation was absorbed on the surface of Frank Lake in the upper layers of the model. The EXH2O coefficient controlled the ability of shortwave solar radiation to penetrate into deep lake strata as it encountered light-absorbing/deflecting components in the water column. An EXH2O value of 1.0 m^{-1} was used, specifying that the shortwave solar radiation that encountered the lake surface was not able to pass into deep strata. To gauge a comparison, an EXH2O value for pure water is 0.25 m^{-1}. Having to regulate the BETA and EXH20 coefficients in the Frank Lake model suggested that the heat distribution in Frank Lake was being largely influenced by the elevated TDS present in the lake, particularly at the surface. The total light extinction present in an aquatic system can be influenced by the water itself (λ_{H2O}), inorganic suspended solids/TDS (λ_{ISS}), particulate organic matter (λ_{POM}), algae/phytoplankton (λ_{a}), zooplankton (λ_{zoo}) and plants/macrophytes (λ_{macro}). The equation below represents how CE-QUAL-W2 develops the total light extinction coefficient given user input.

$$\lambda = \lambda_{H2O} + \lambda_{ISS} + \lambda_{POM} + \lambda_{a} + \lambda_{macro} + \lambda_{zoo}$$

In the current Frank Lake model, computations for total suspended solids, phytoplankton, zooplankton and macrophytes were not performed because no data was input for these constituents. Recall that phytoplankton growth in Frank Lake was suggested by the chl *a* trends discussed in Chapter 1 and live zooplankton specimens were found within Frank Lake samples. The presence of these organisms in Frank Lake meant that they were also contributing to light shattering and extinction in the upper water column. This helped to explain the need for such a large adjustment of both the BETA and EXH2O coefficients from the default values of 0.45.

A further complication regarding light extinction in Frank Lake was the water colour variable, which has been changed by the effluent. Both the current study and a previous consultant study found that in general, the effluent discharged into Frank Lake has diluted the dissolved organic carbon (DOC) within the lake and made the water more clear (LePage and Russel 2013). However, the late date of discharge initiation and the substantial inputs of run-off and natural inflow into Frank Lake in 2013 increased the dissolved organic carbon (DOC) in the lake, particularly at the lake surface (Figure 1.61, Appendix A). The humic and fulvic acids measured as DOC are associated with the brown colouration of natural waters (Morris *et al* 1995, Poniewozik *et al* 2011). Light extinction can be largely affected by brown-coloured water and its DOC components by decreasing the permeation of light into deeper strata (Hem 1960*a*, Morris *et al* 1995, Verduin 1982).

To summarize, TDS, phyto- and zooplankton as well as increased DOC in Frank Lake in 2013 all contributed to prevention of the light penetration into deep strata in Frank Lake and hence, adjustment of the appropriate coefficients was required.

Possible Calibration Improvement Strategies

There are a multitude of improvements that can be made to the calibration of the Frank Lake model regarding both temperature and TDS calibrations. Regarding the water balance deviations, it is possible that the characterization of the head vs. flow relationship developed for the beaver dam/spillway at the outlet could be improved such that flow becomes greater when upstream head/water level within the Frank Lake is high. Revisiting the algorithm associated with the spillway could improve the water balance within the model. The Water Balance Utility was designed as an external feature to the CE-QUAL-W2 model and allows for calculation of deviations between model predictions and field data. Deficiencies or excesses in water level can be adjusted by using tributaries (if the model is lacking water) or pumps (if the model has too much water). The ability of this utility to help with the water balance is only effective to a point but its effectiveness should be investigated for the Frank Lake model. If a tributary or pump is used to improve the water balance, the location and associated TDS concentration of each will have to be logically designed and such that improvements to the TDS calibration will ensue. In addition, no precipitation TDS data was available and an estimated value was used. Experimentation of the precipitation TDS concentration could potentially improve TDS calibrations as well.

As mentioned, the EXH2O and BETA coefficients are a function of the suspended substances in the water column (both dissolved and particulate). Since the TDS concentrations in Frank Lake varied greatly (particularly at the lake surface) as a result of the May 2013 rain event and effluent discharge starting in June 2013, it is possible that the EXH20 and BETA appropriate for the lake varied over time. CE-QUAL-W2 has been designed such that an input file for a time-varying EXH2O is possible. This was originally designed because as phytoplankton and macrophytes grow throughout the year, the light absorption at the surface changes. Development of a time-varying light extinction input file for Frank Lake may help to improve model projections of temperature and possibly TDS in Frank Lake.

There are a number of settings in the model that can allow for adjustment of density and how it relates to the placement of inflows into the model grid and thus, a sensitivity analysis to test some of these options needs to occur.

Simulation Scenarios and Frank Lake Meromixis

One year simulation scenarios were used to test Frank Lake's response to decreased TDS concentrations supplied to the lake at the inlet using reductions of 10%, 25%, 50% and 75% reduction scenarios were performed. The chemocline depths were not largely impacted by the 10% and 25% scenarios however, the chemocline depth was found to be closer to the surface in the 50% and 75% reduction scenarios. In addition, much greater dilution occurred near the lake's surface in the 50% and 75% scenarios. The shallowing of the chemocline in these scenarios indicated an increase in meromictic stability and a shallower depth of fall turnover in Frank Lake. This was a similar occurrence to what happened in Lim Lake where an abrupt reduction in inflowing TDS concentration promoted meromictic stability. In all scenarios, no change in the monimolimnion TDS concentrations occurred. Essentially, regardless of what sort of TDS reduction were to occur at the inflow of Frank Lake, it will not work to deteriorate meromictic stability in Frank Lake over a one year timeframe.

Few published studies have attempted to model meromictic trends with CE-QUAL-W2 with the goal of trying to quickly and successfully destabilize the chemocline using inflow water quality. In the study performed for Kennady Lake where meromictic stability was attempting to be maintained, it was found that meromictic stability was established very quickly after closure and was maintained in the model for up to 100 years (Herrell *et al* 2015, Vandenberg *et al* 2015). The large difference between the Kennady Lake and Frank Lake is that Kennady Lake has large surpluses of high TDS groundwater draining to it, which enhanced and maintained its meromictic stability in the model (Herrell *et al* 2015). Other past studies not involving modeling that have studied meromictic stability trends all found that meromictic stability deterioration occurred in the study lake(s) because some mechanism equalized or brought the dissolved solids concentrations close enough together in the upper and lower strata to promote mixing (Jellison *et al* 1998, Romero and Melack 1996).

Unlike Lim Lake during its effluent receiving years, Frank Lake has had long-term and stable meromixis, even during the years of receiving effluent. This fact suggests that it is unlikely that turnover in Frank Lake will occur as a result surface strata TDS concentrations increasing enough from effluent discharge to equalize with bottom strata concentrations. The Frank Lake watershed captures too much dilution water and the lake is too deep for this to occur. The deterioration of meromictic stability in Frank Lake will likely occur via a slow descent of the chemocline towards the bottom of the lake as wind mixing slowly lifts chemical constituents up from the monimolimnion into the mixolimnion (Hutchinson 1957). Initially, this process requires less work since the chemocline is closer to wave action, however, as the chemocline drops, its protection from wind increases and there is a tendency for its stability to increase (Hutchinson 1957, Walker 1974). It is possible that this stability increase will be minimal since as the chemocline drops, the surface area and volume of the monimolimnion also decreases and therefore less work is required to mix the remaining monimolimnion strata with the mixolimnion (Hutchinson 1957). As discussed in Chapter 1, the removal of sulphate from the water column will likely become more apparent after effluent discharge ceases. Sulphate allocation to the sediments as both inorganic (sulphides) and organic sulphur forms will prompt long and short term sulphur storage and will act as a TDS-reduction mechanism in the monimolimnion of Frank Lake (Carignan and Tessier 1988, Giblin *et al* 1990, Kling *et* al 1991, Rudd *et al* 1986, Nriagu and Soon 1985). This coupled with dilution in the mixolimnion waters will be the main mechanisms by which Frank Lake's meromixis deteriorates.

Future Modeling Scenarios

Long-term scenarios examining Frank Lake's meromictic stability are required. Currently, a long-term post-closure management plan had been designed for Frank Lake and input TDS and potentially flow files can be developed to represent how the lake will respond to the plan. The 5%, 10%, 25%, 50% and 75% reduction scenarios performed in the current study were only a start of possible scenarios that could be considered now that the model is appropriately calibrated. All other boundary condition data will be kept constant during such scenarios. A great level of confidence could be placed in the model if more years of data are collected and model calibration can be performed with other data sets, especially if those new calibration data sets encompassed different boundary conditions experienced by Frank Lake (dry year, wet year, year without effluent discharge etc.). For these long-term scenarios, the physical and chemical data collected at the inflow of Frank Lake prior to the discharge period will be used to represent the type of water quality flowing into the lake after mine closure since this is the best representation of "natural inflow" into the lake currently available.

Conclusion

If TDS concentrations in the surface strata in Frank Lake are allowed to dilute substantially as suggested by the 50% and 75% scenario results and based on the results of the Kennady Lake study, the meromictic stability in the lake will be strengthened and the meromictic state of the lake will likely be prolonged. The addition of successively lowered TDS into Frank Lake from the Hemlo site could cause the TDS concentration in the mixolimnion to slowly decrease overtime rather than rapidly dilute from precipitation and run-off as was observed in Lim Lake. Continuing to keep the TDS concentration in the mixolimnion slightly elevated could allow turnover events, especially in the fall, to be more effective at breaking down the chemocline, since the chemical stability between the mixolimnion and monimolimnion will not be increased by the presence of a highly-diluted mixolimnion. However, if elevated TDS concentrations still remain in Frank Lake after the long-term post-closure management strategies have occurred, meromictic conditions still have the potential to develop. If such a scenario occurred and Frank Lake's TDS concentrations are above natural inflow concentrations, dilution of the surface water in Frank Lake is certain to occur and the potential for the development of a mixolimnion remains.

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Appendix A: Figures

Figure 1.1. Location of Barrick's Hemlo Gold Mine in Ontario (adapted from Orr and Stecko 2006).

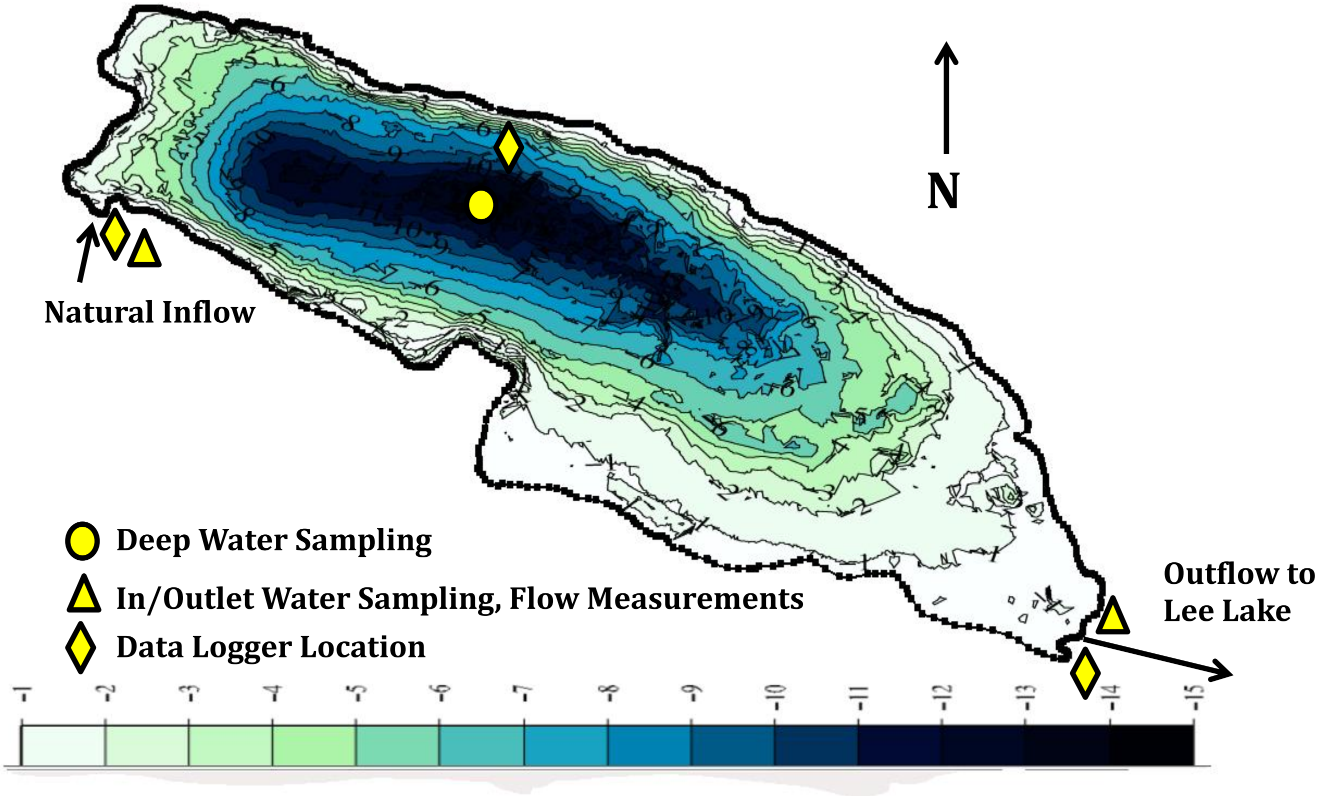


Figure 1.2. Water sampling and data logger locations in Lim Lake.

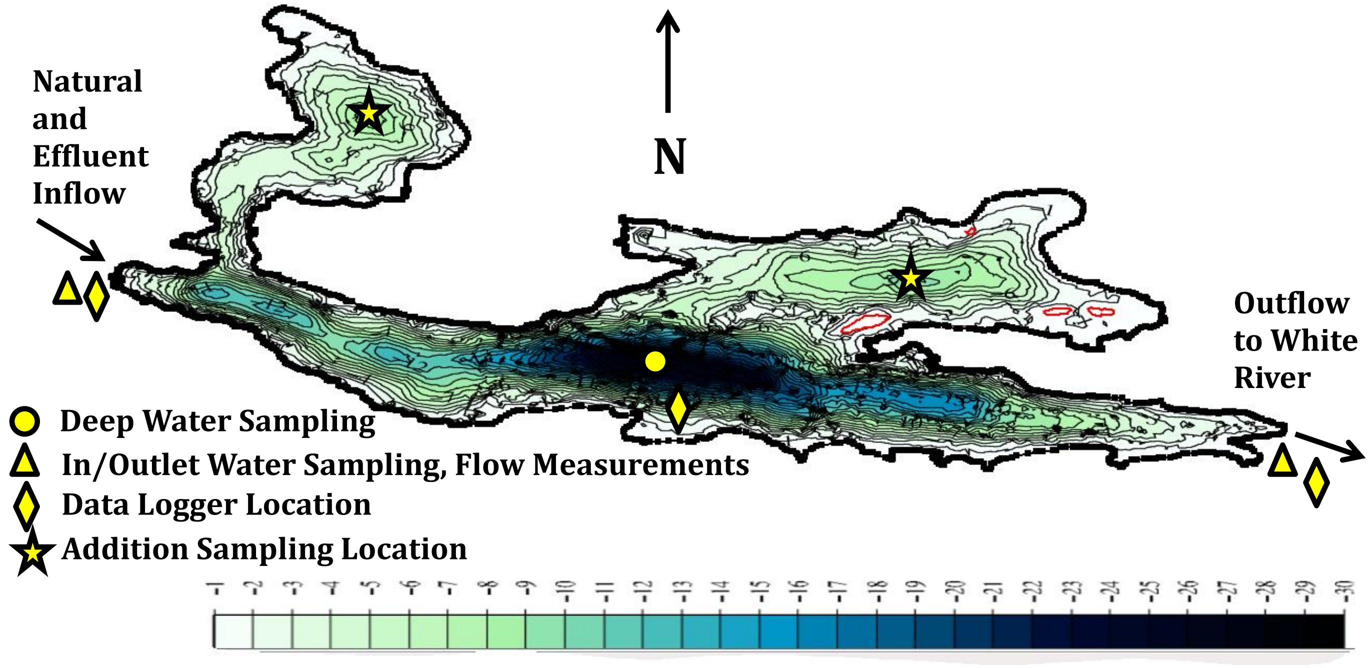


Figure 1.3. Water sampling and data logger locations in Frank Lake.

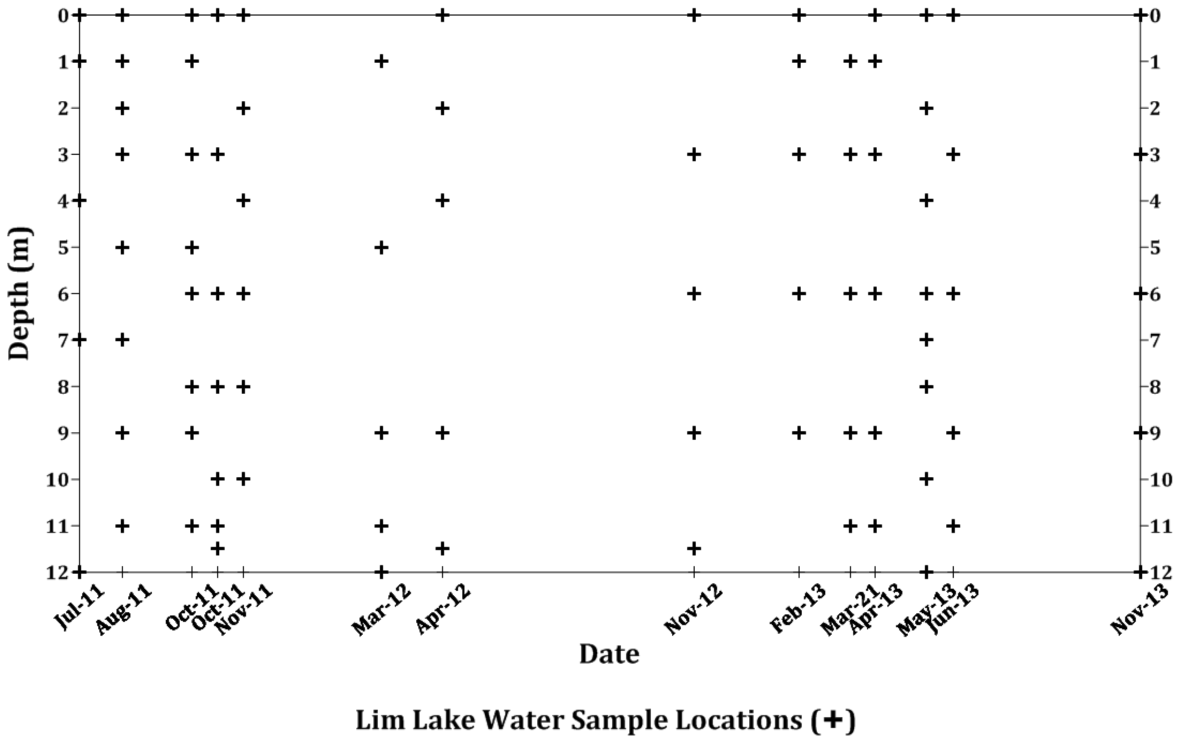


Figure 1.4. Lim Lake sample locations at depth (+) for sample sessions in Jul 2011-Nov 2013.

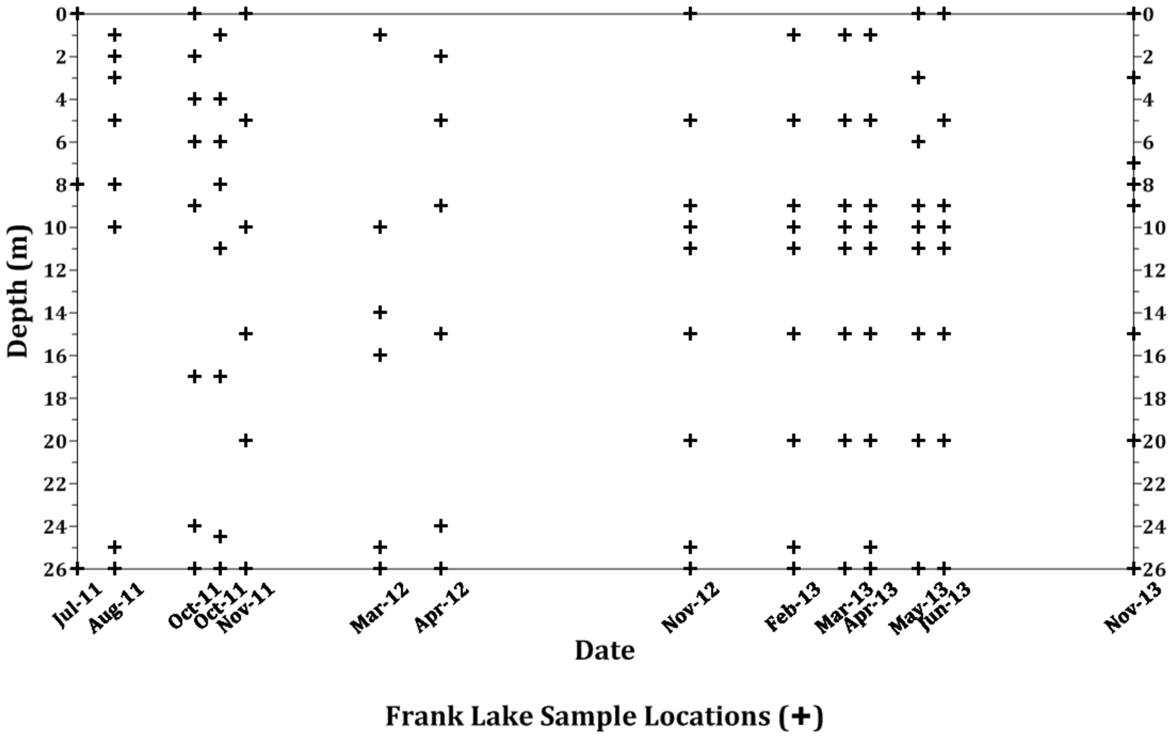


Figure 1.5. Frank Lake sample locations at depth (+) for sample sessions in Jul 2011-Nov 2013.

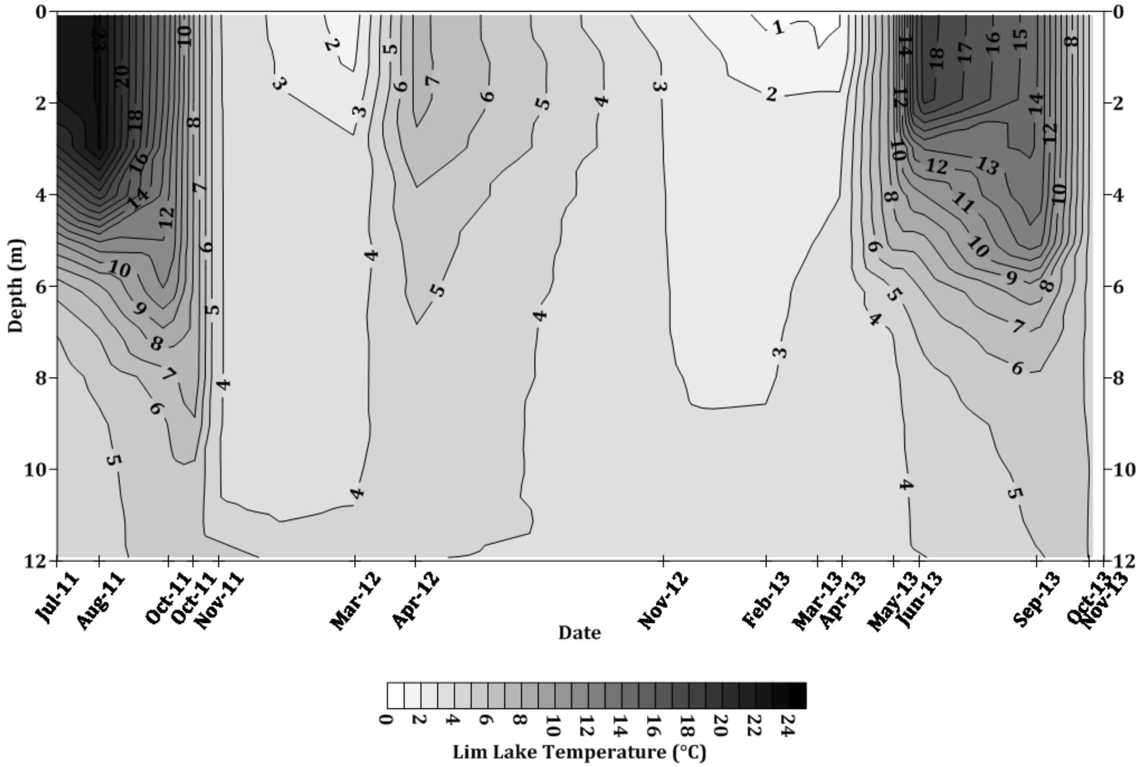


Figure 1.10. Lim Lake temperature (°C) profiles from Jul 2011-Nov 2013.

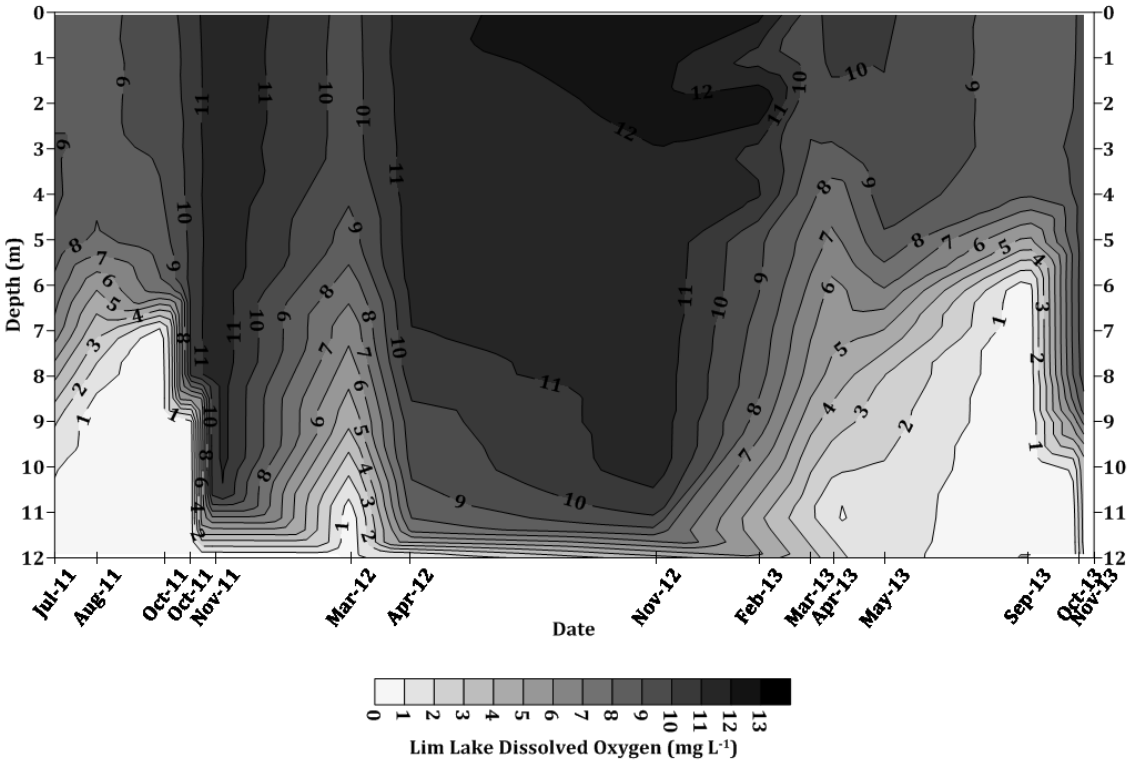


Figure 1.11. Lim Lake dissolved oxygen (mg L^{-1}) profiles from Jul 2011-Nov 2013.

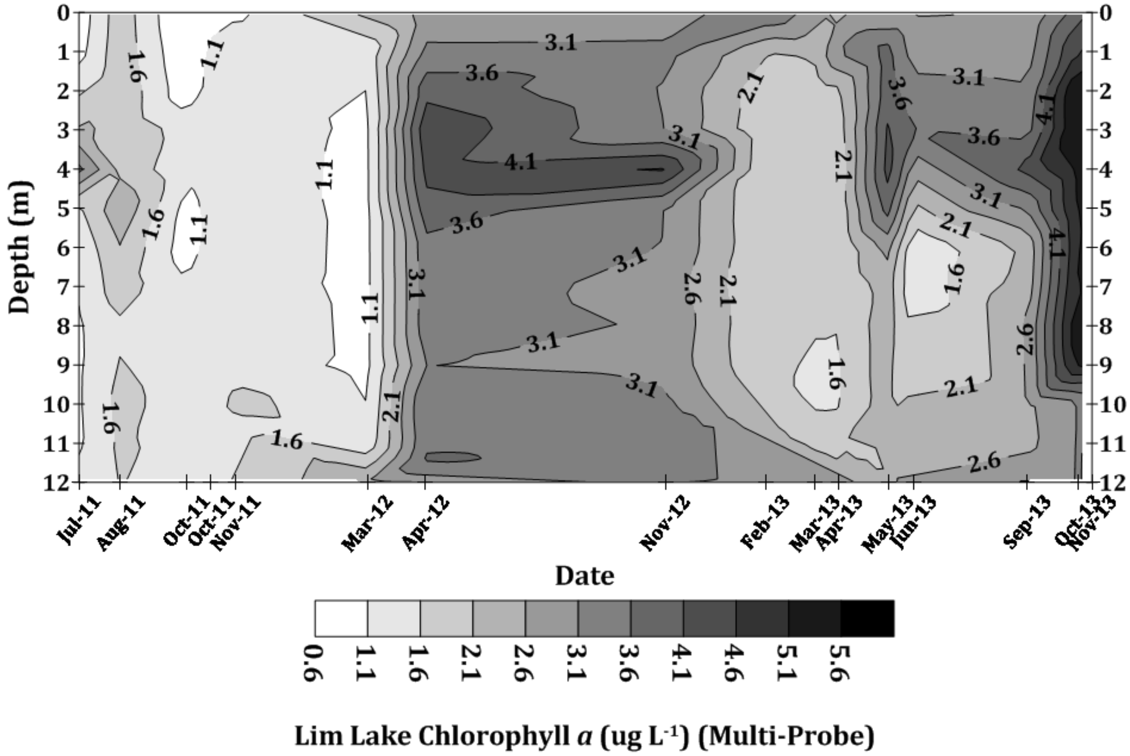


Figure 1.12. Lim Lake chlorophyll *a* (µg L^{-1}) multi-probe profiles from Jul 2011-Nov 2013. Jun 2013 data from lab extractions at 0, 3 and 6 m.

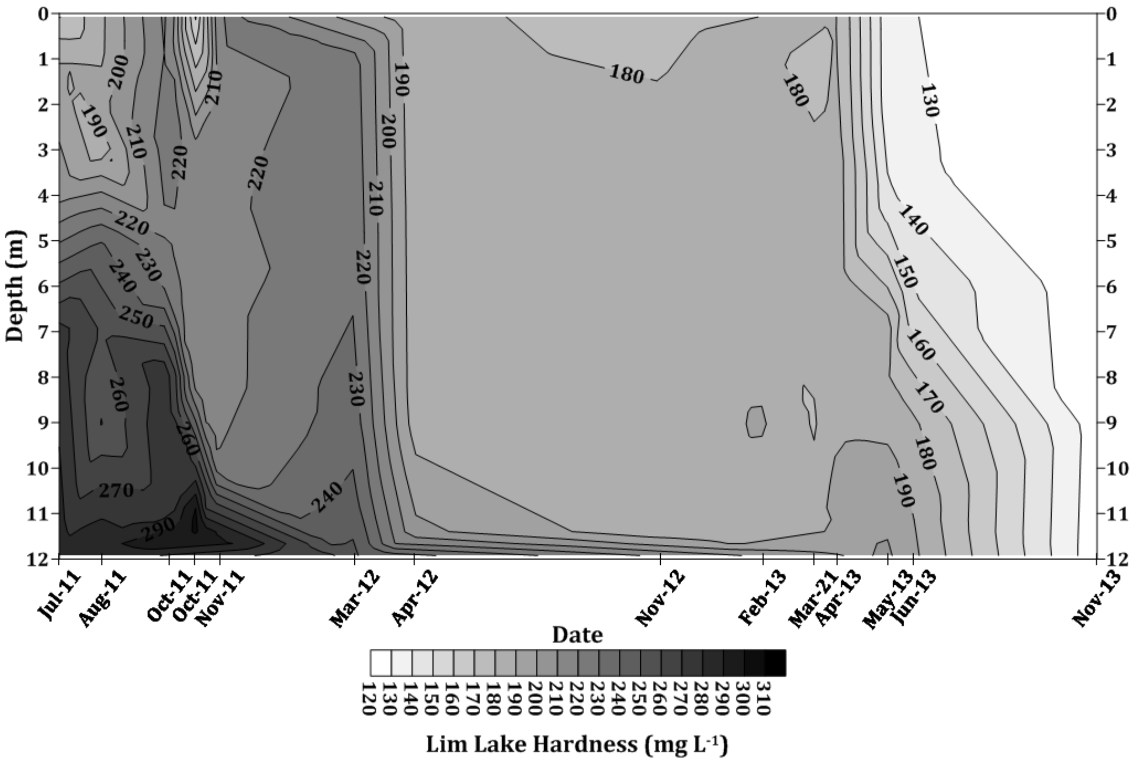


Figure 1.13. Lim Lake hardness (mg L^{-1}) profile calculations from Jul 2011-Nov 2013.

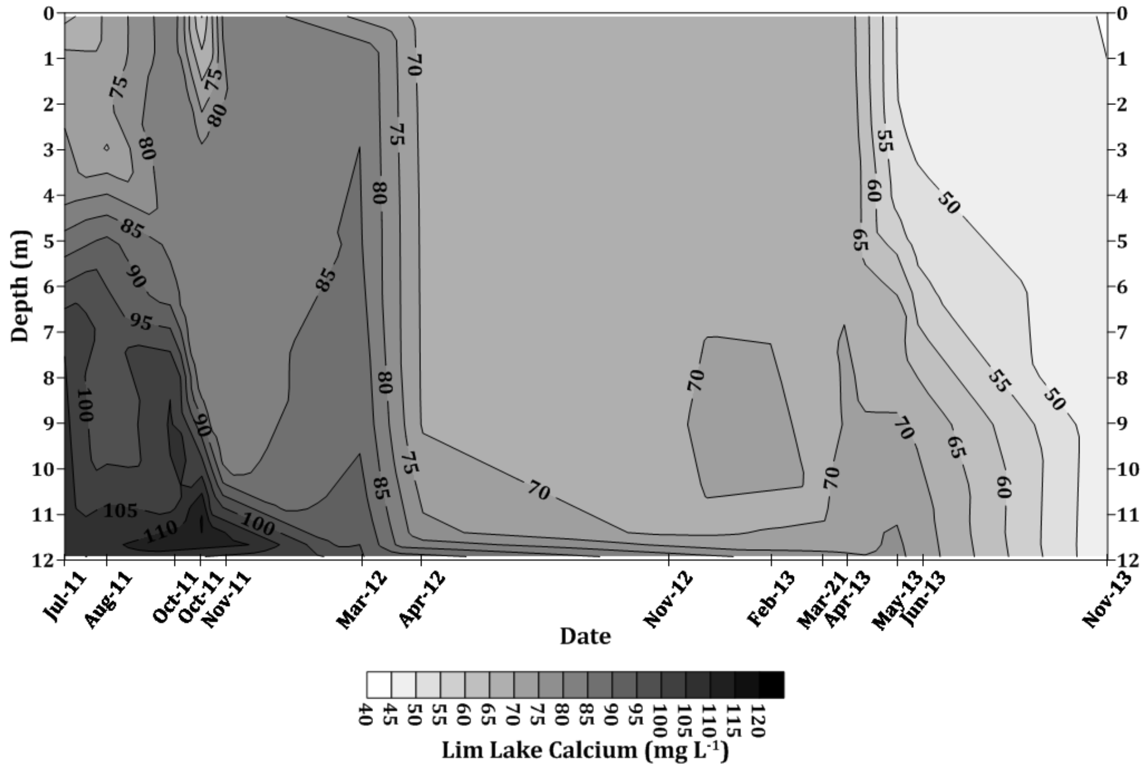


Figure 1.14. Lim Lake calcium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

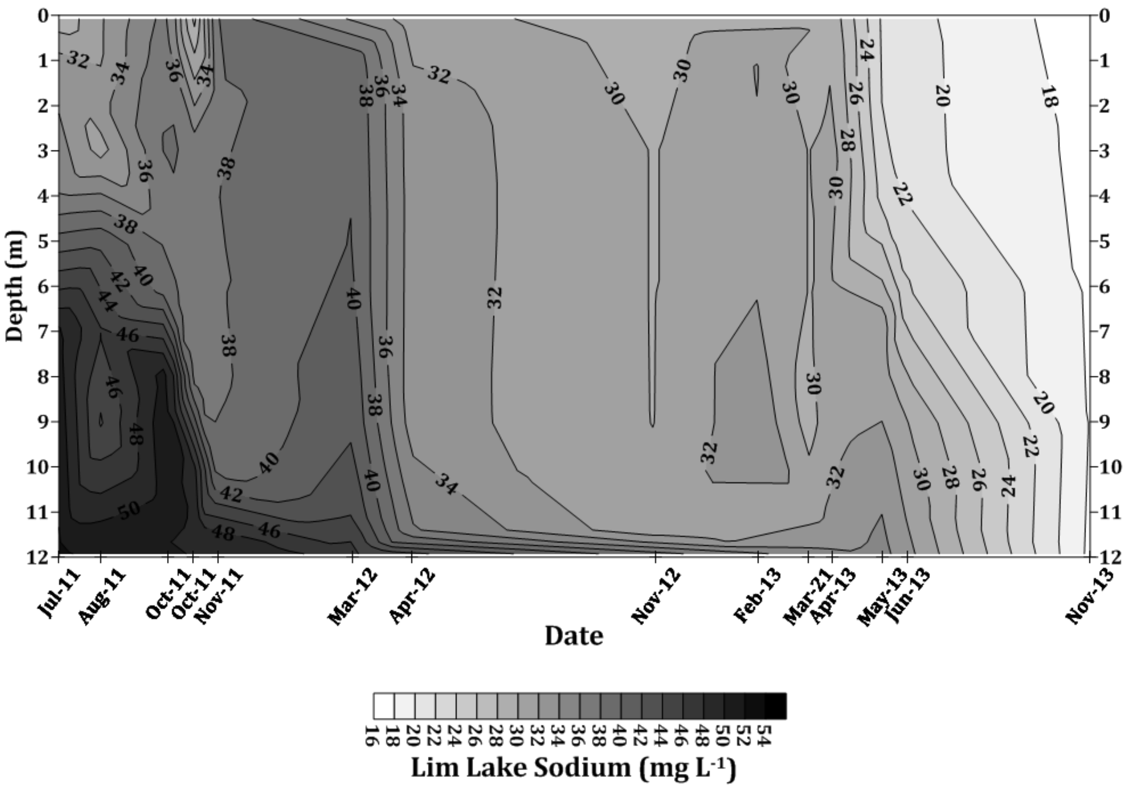


Figure 1.15. Lim Lake sodium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

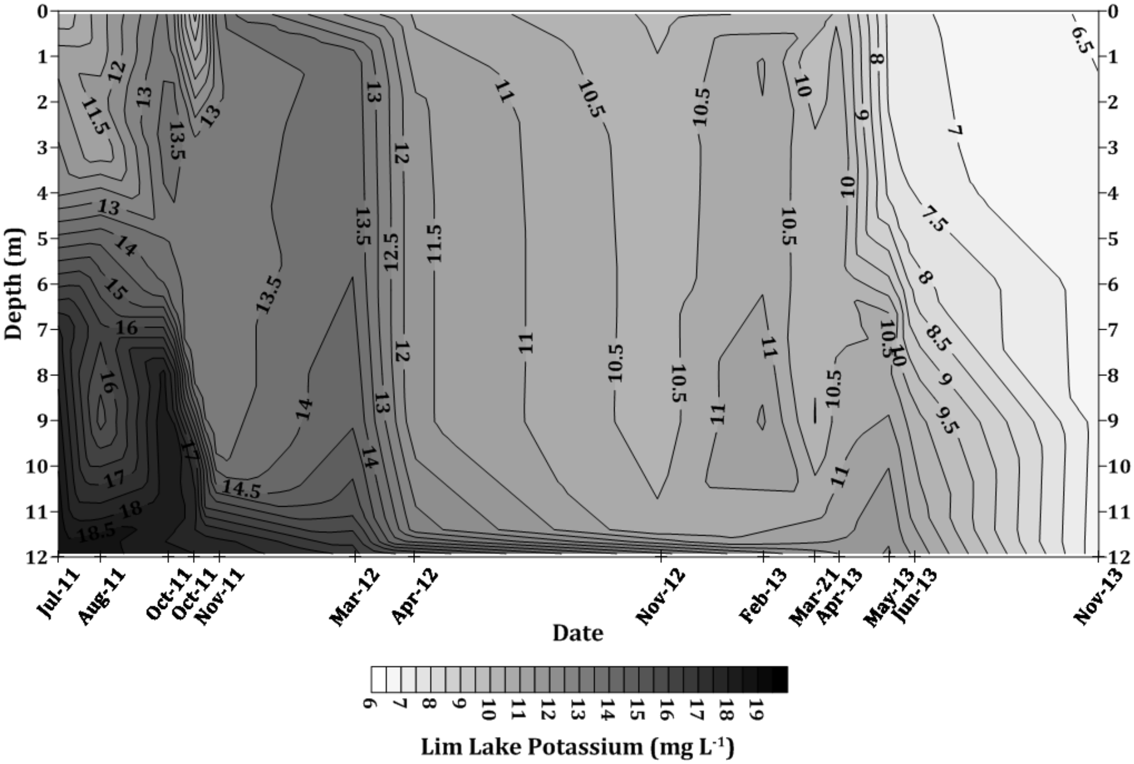


Figure 1.16. Lim Lake potassium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

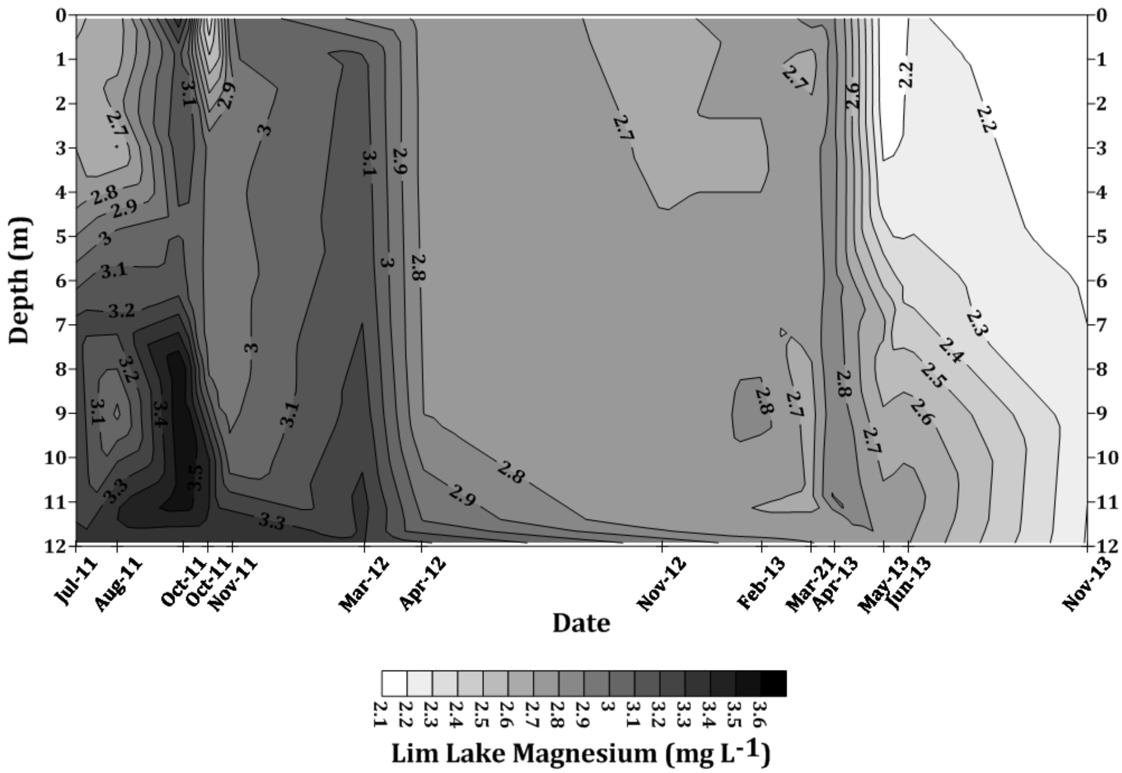


Figure 1.17. Lim Lake magnesium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

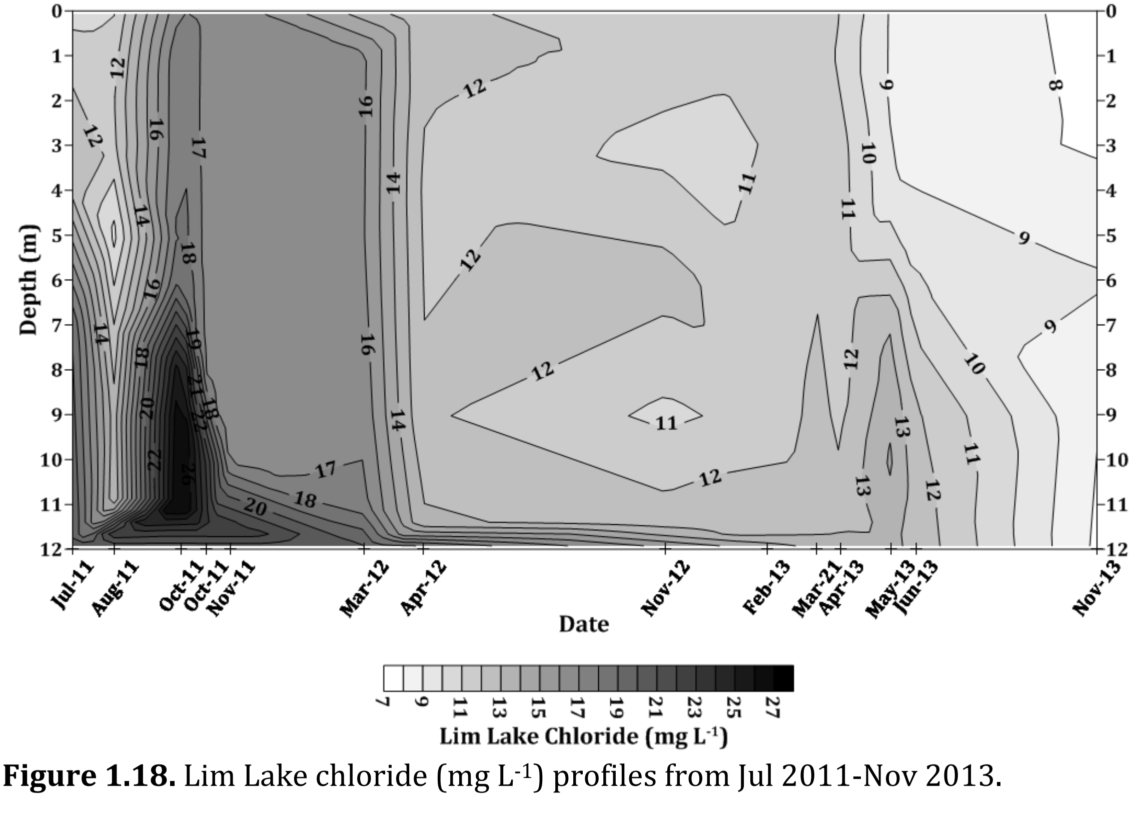


Figure 1.18. Lim Lake chloride (mg L^{-1}) profiles from Jul 2011-Nov 2013.

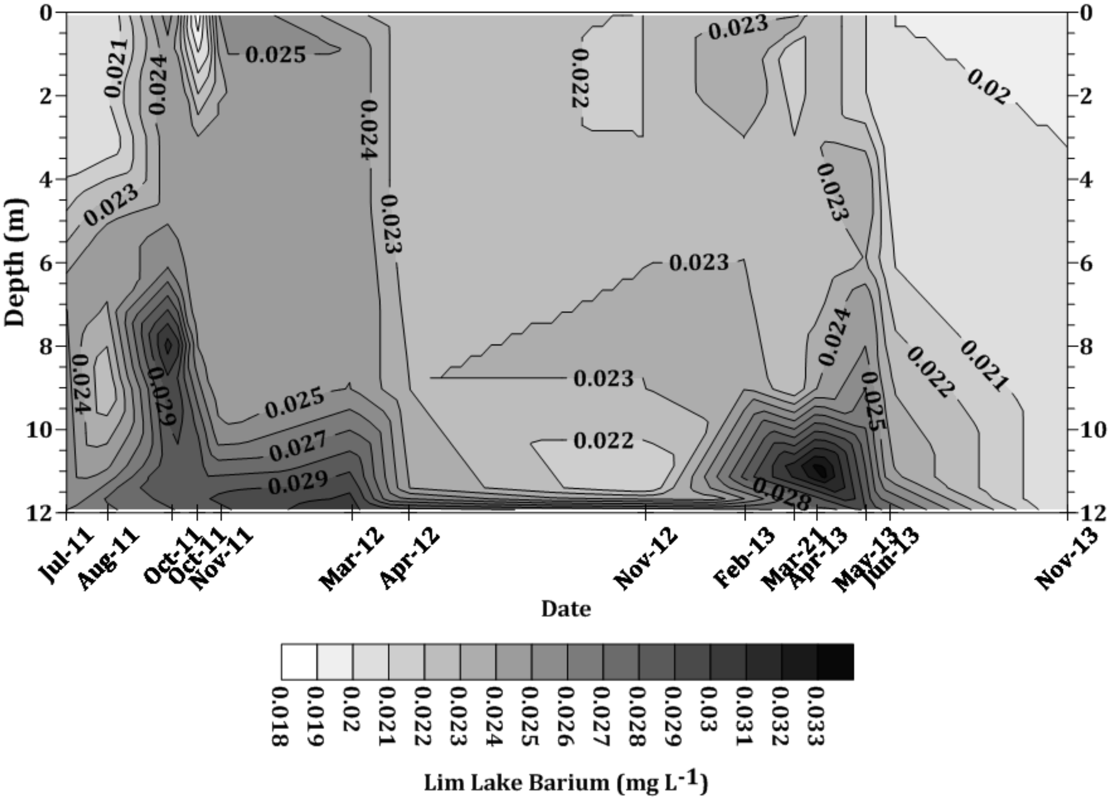


Figure 1.19. Lim Lake barium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

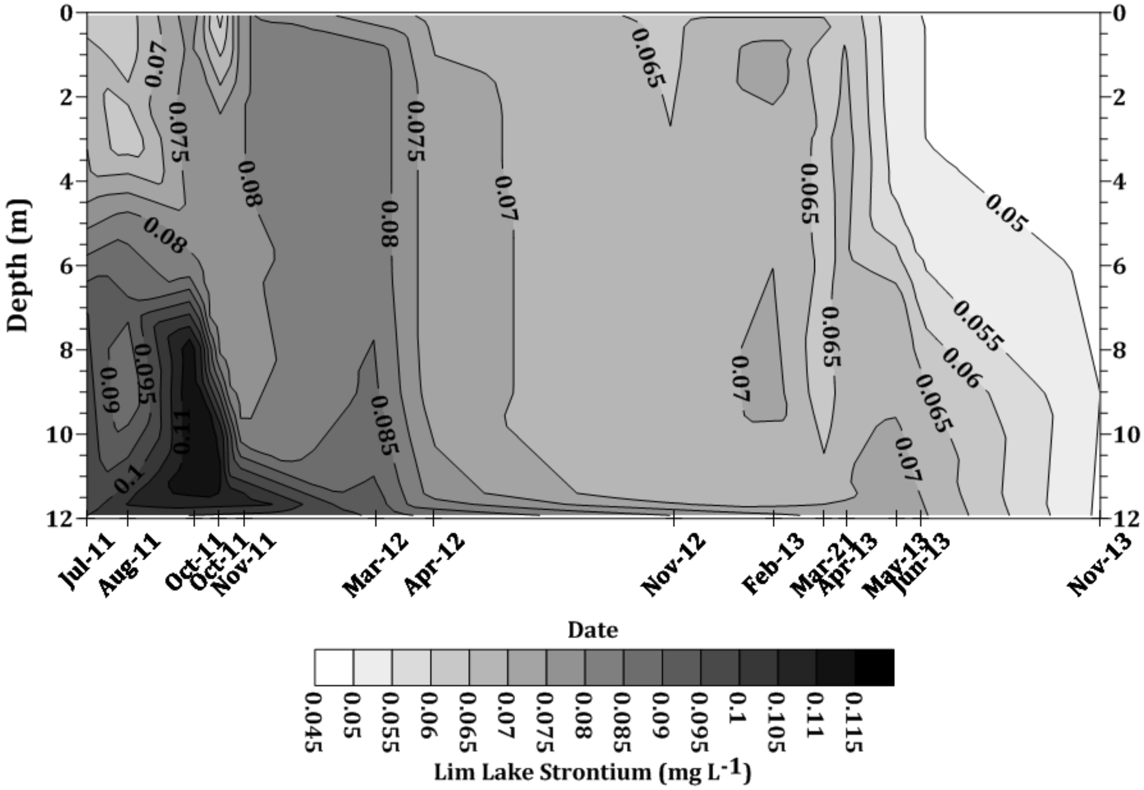


Figure 1.20. Lim Lake strontium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

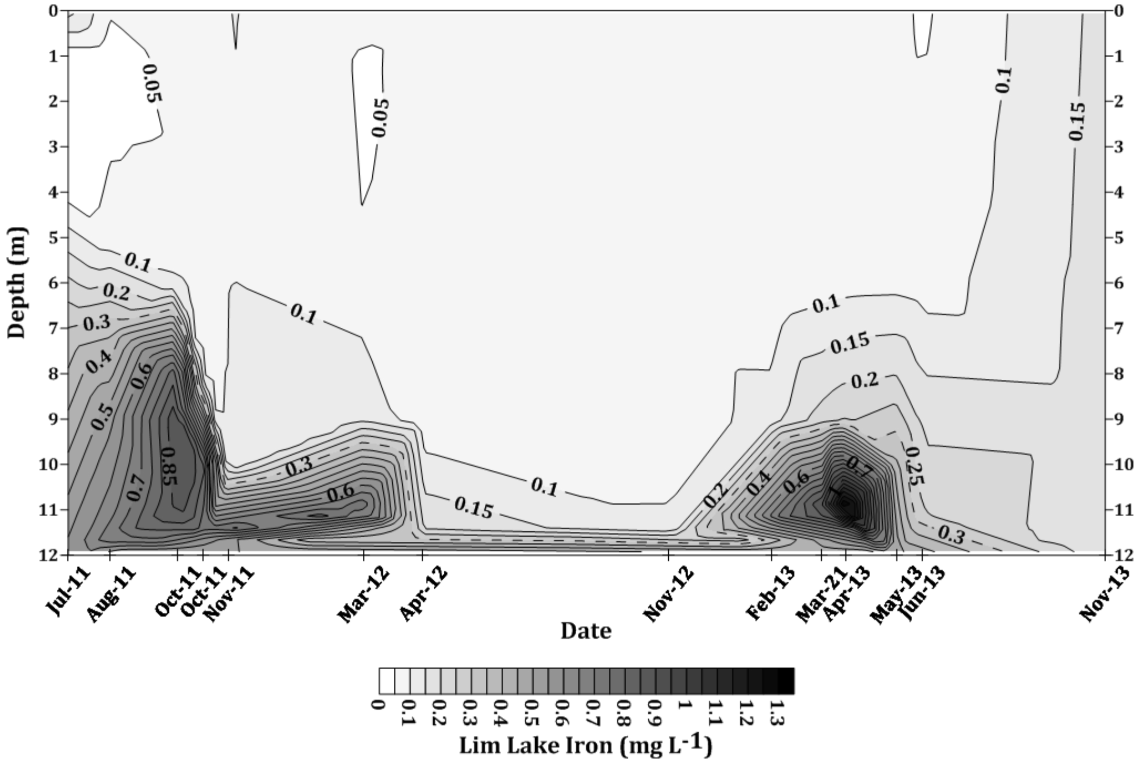


Figure 1.21. Lim Lake iron (mg L^{-1}) profiles from Jul 2011-Nov 2013. Dashed contour = PWQO (0.30 mg L^{-1}).

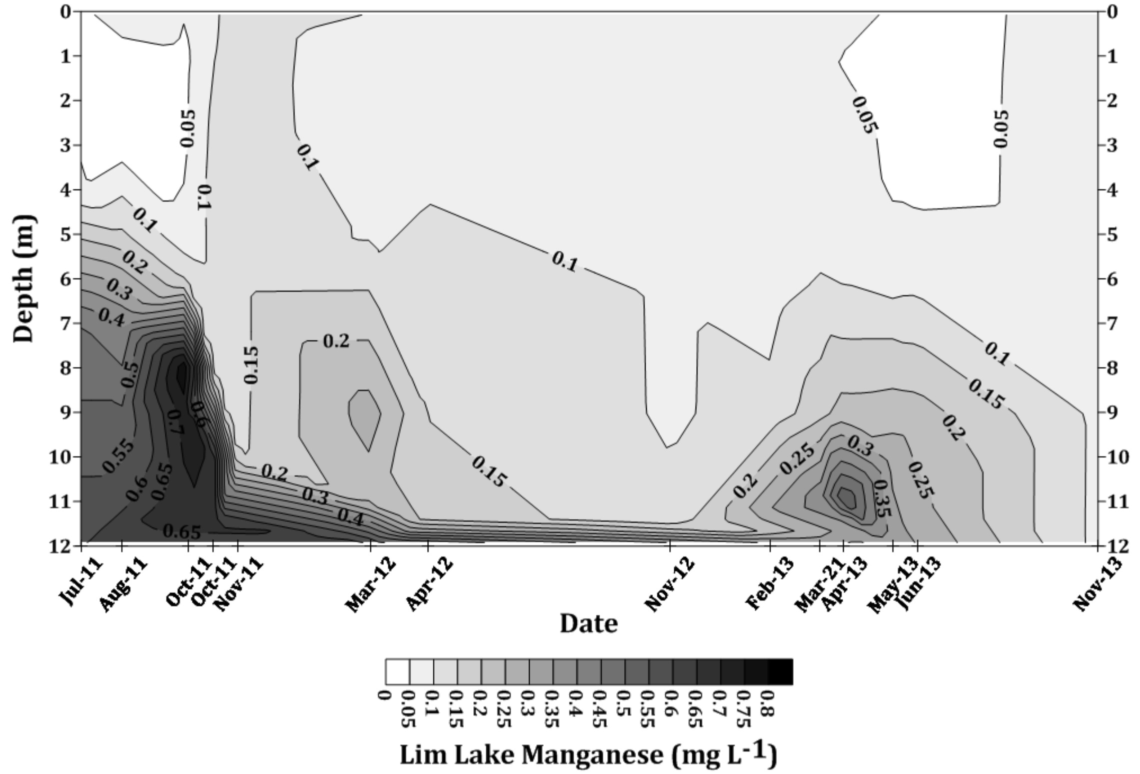


Figure 1.22. Lim Lake manganese (mg L^{-1}) profiles from Jul 2011-Nov 2013.

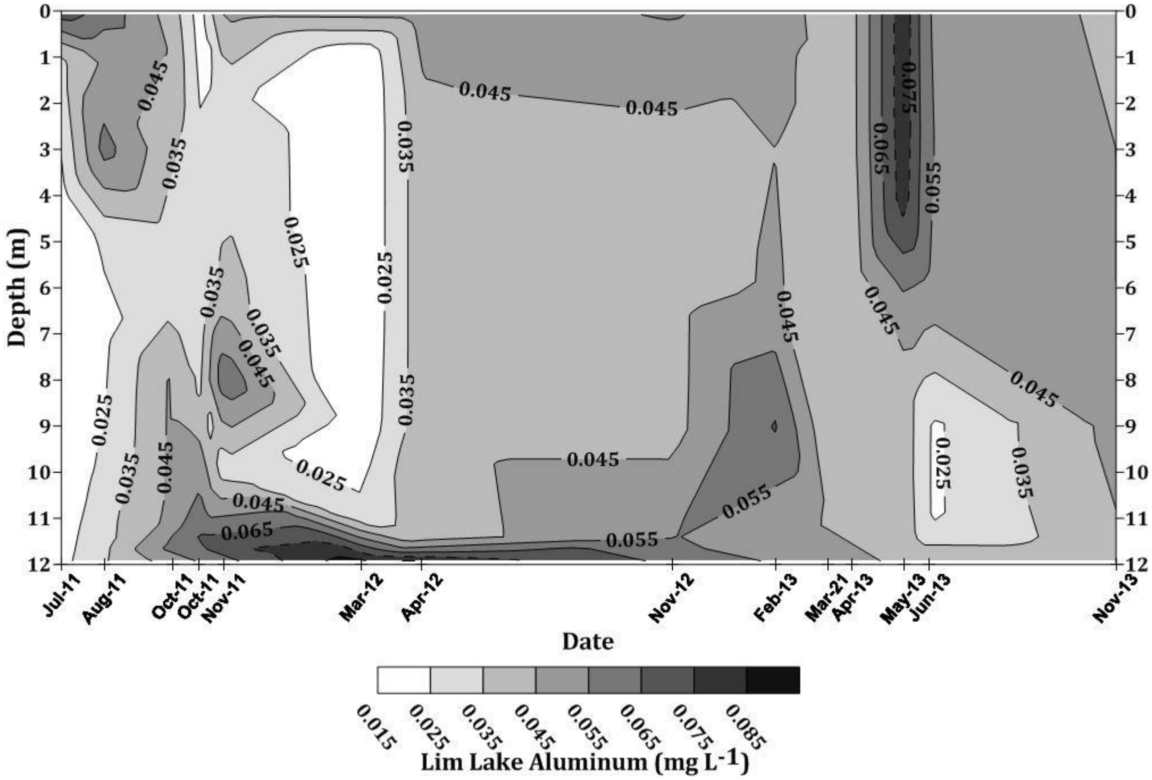


Figure 1.23. Lim Lake aluminum (mg L^{-1}) profiles from Jul 2011-Nov 2013. Dashed contour = PWQO (0.075 mg L^{-1}).

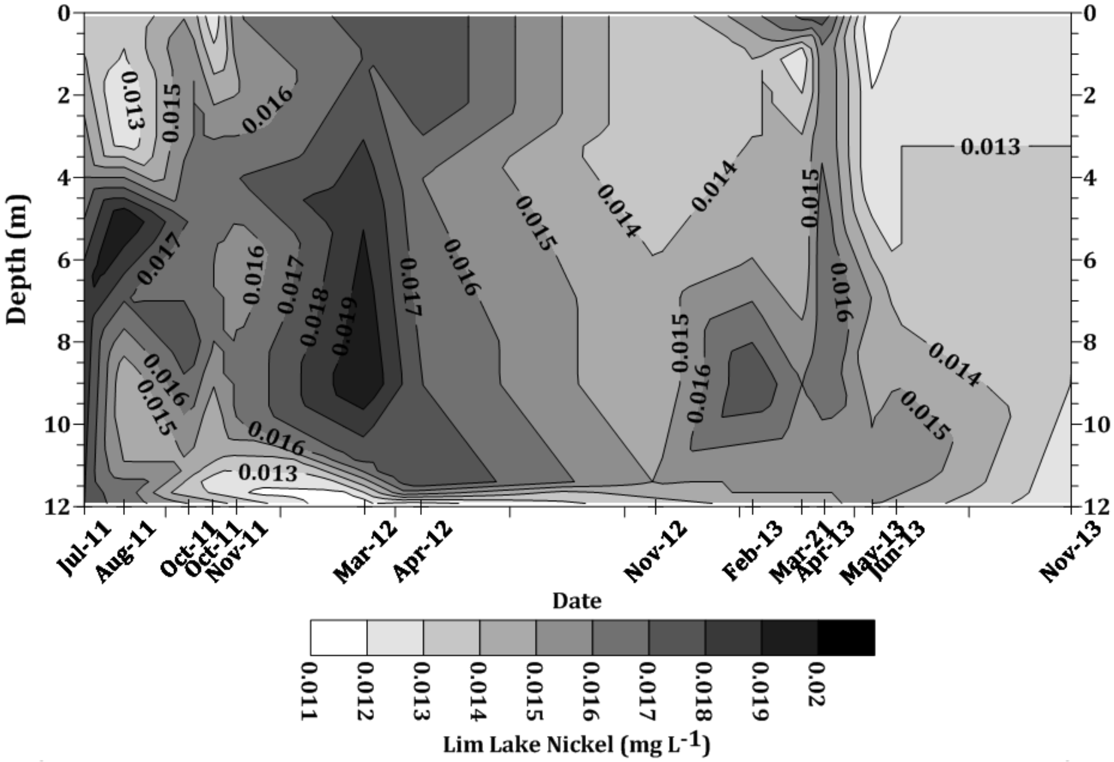


Figure 1.24. Lim Lake nickel (mg L^{-1}) profiles from Jul 2011-Nov 2013.

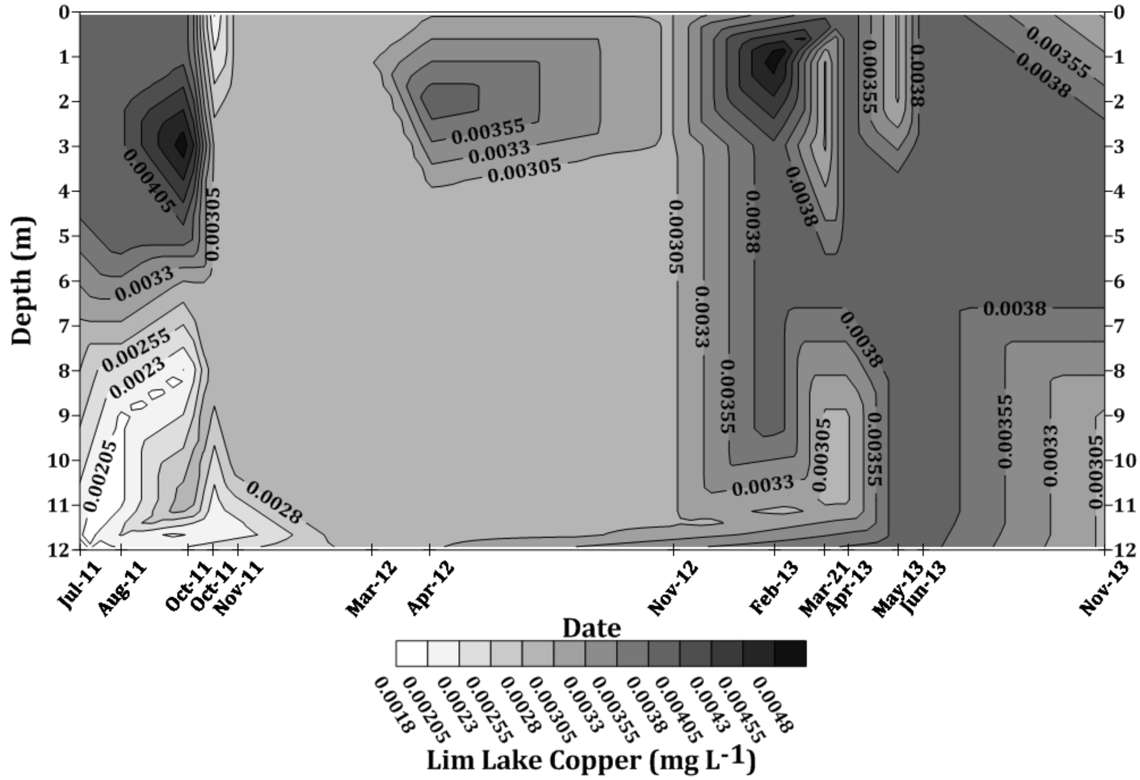


Figure 1.25. Lim Lake copper (mg L^{-1}) profiles from Jul 2011-Nov 2013.

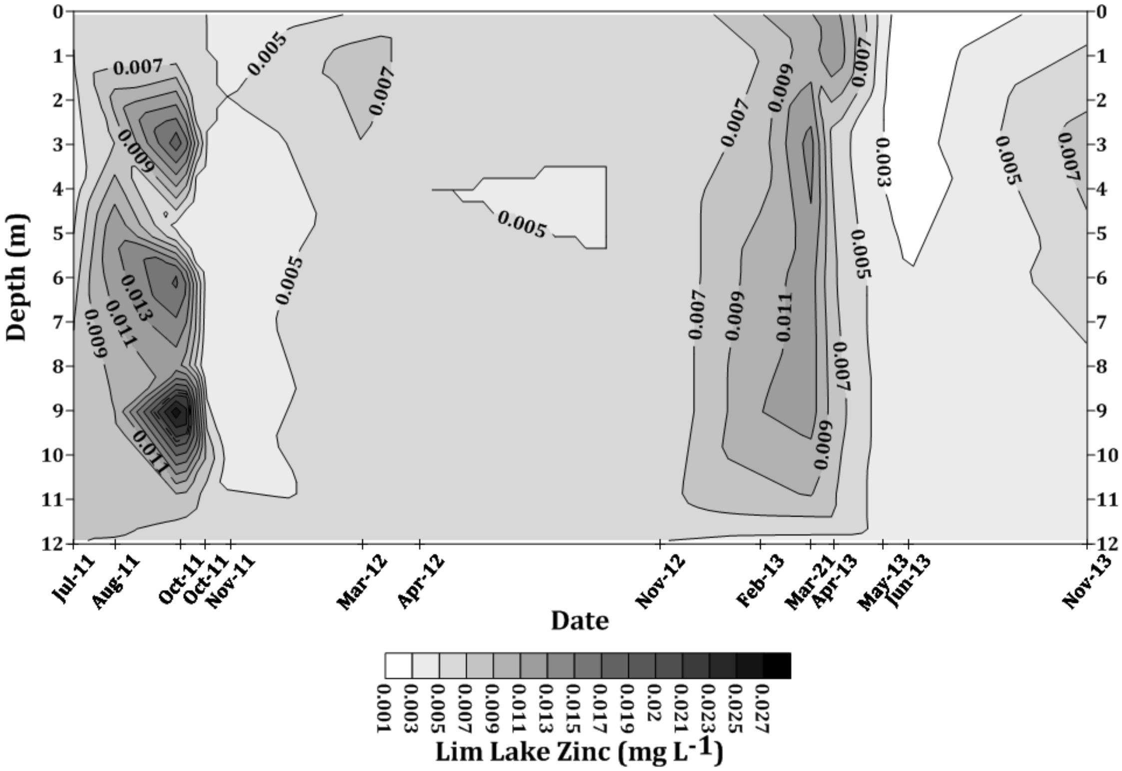


Figure 1.26. Lim Lake zinc (mg L^{-1}) profiles from Jul 2011-Nov 2013. Dashed contour = PWQO (0.020 mg L^{-1}).

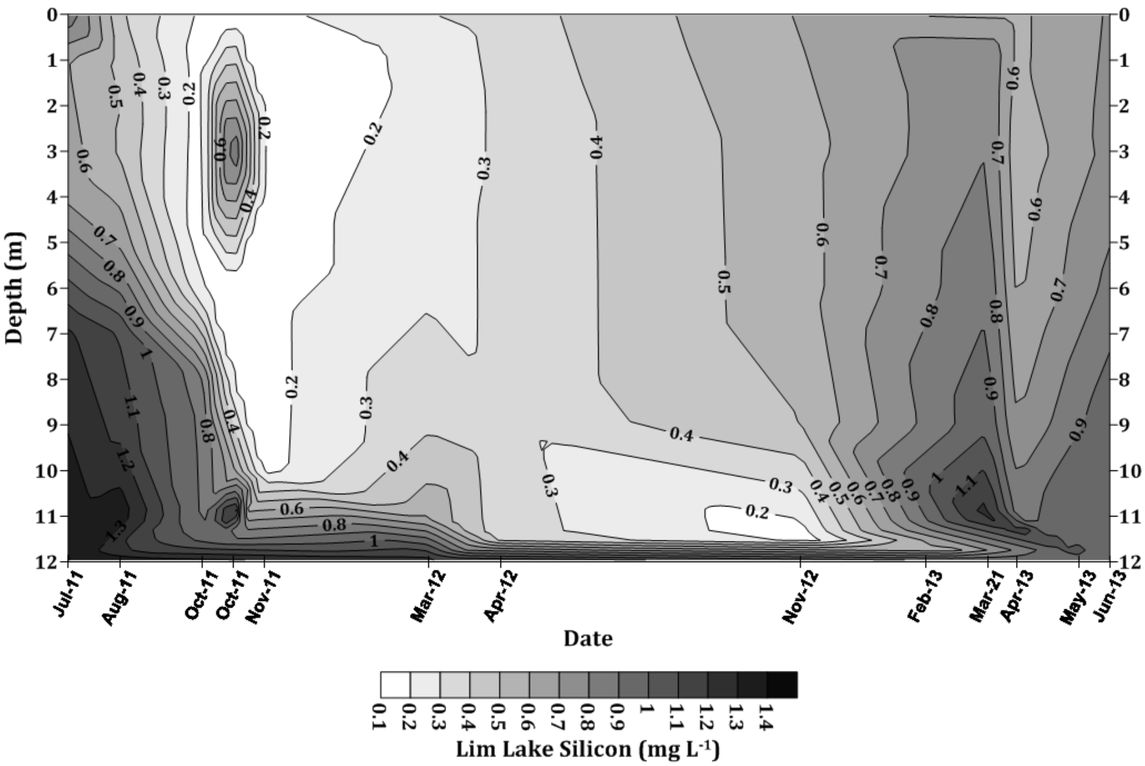


Figure 1.27. Lim Lake silicon (mg L^{-1}) profiles from Jul 2011-Jun 2013.

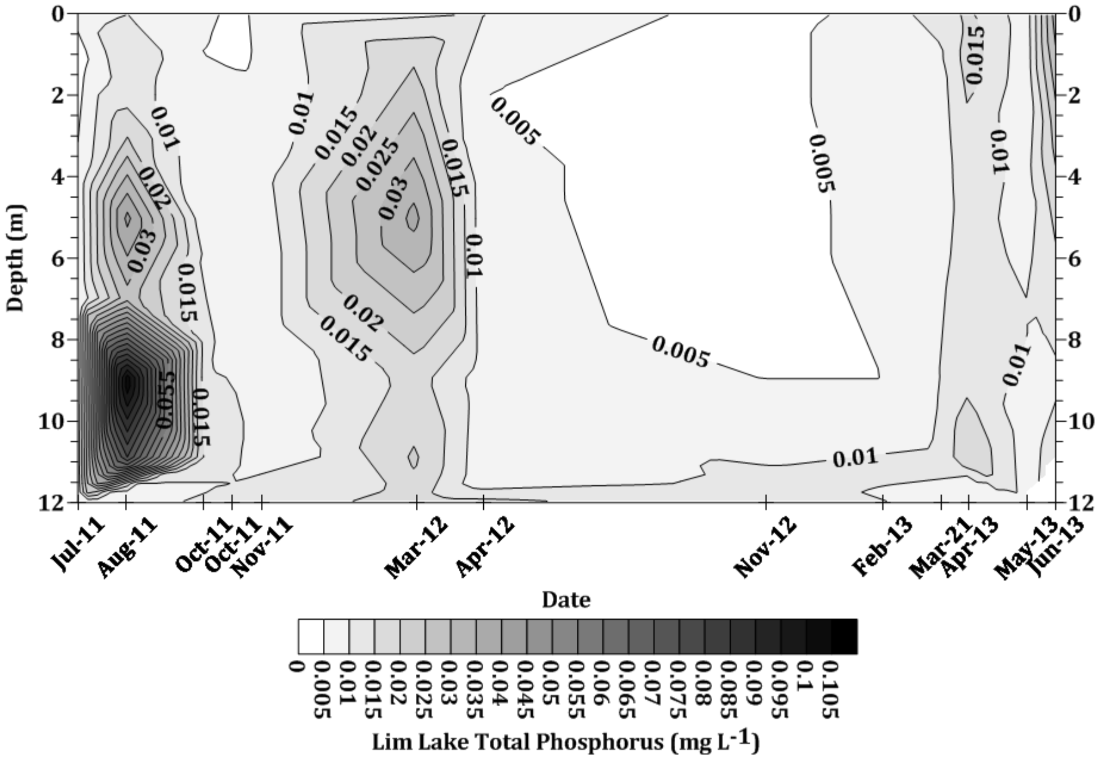


Figure 1.28. Lim Lake total phosphorus (mg L^{-1}) profiles from Jul 2011-Nov 2013.

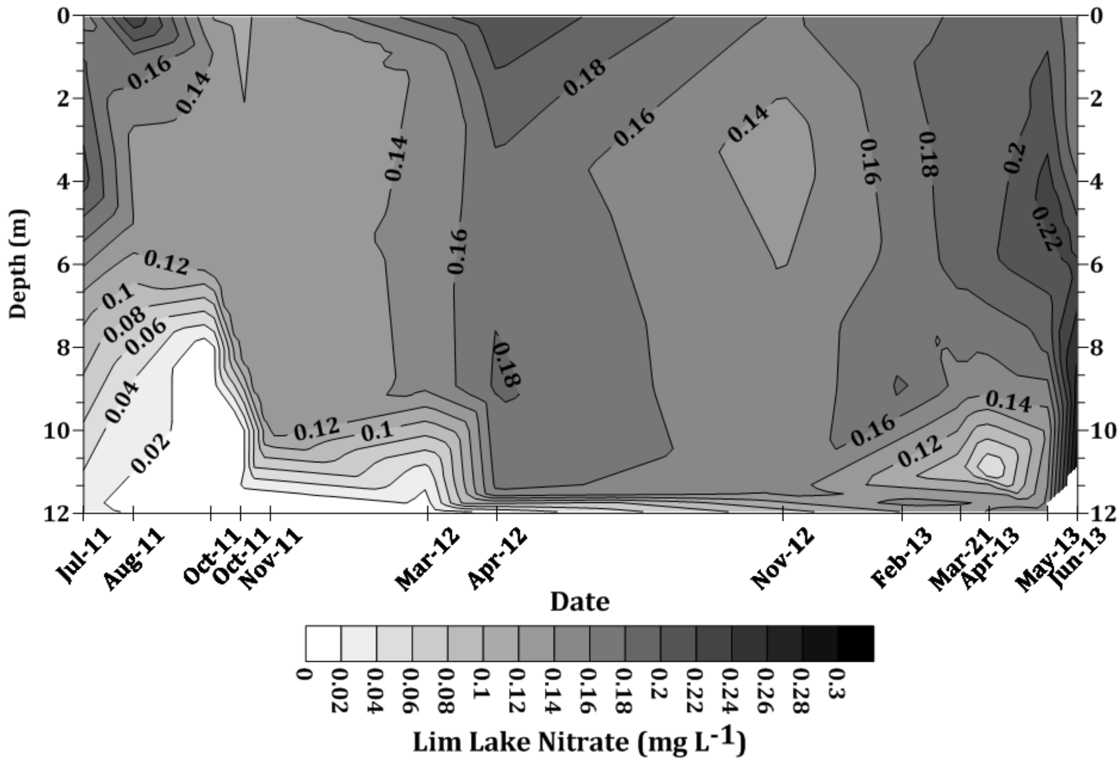


Figure 1.29. Lim Lake nitrate (mg L^{-1}) profiles from Jul 2011-Nov 2013.

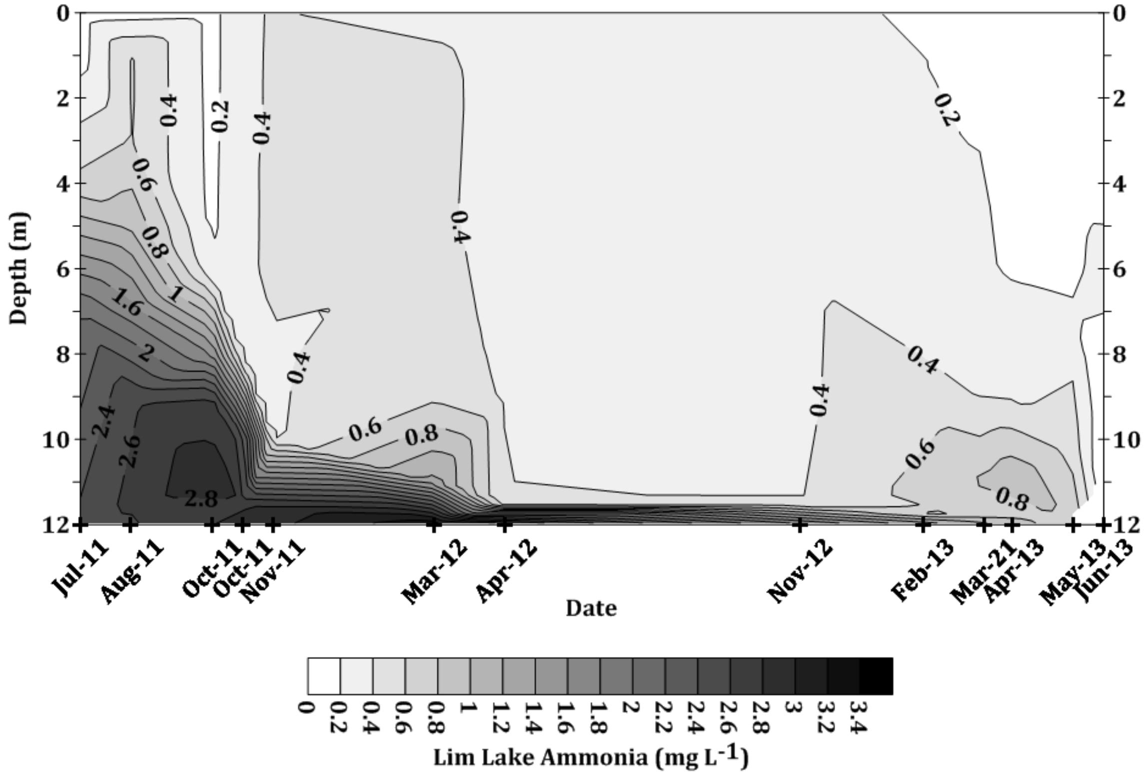


Figure 1.30. Lim Lake ammonia (mg L^{-1}) profiles from Jul 2011-Jun 2013.

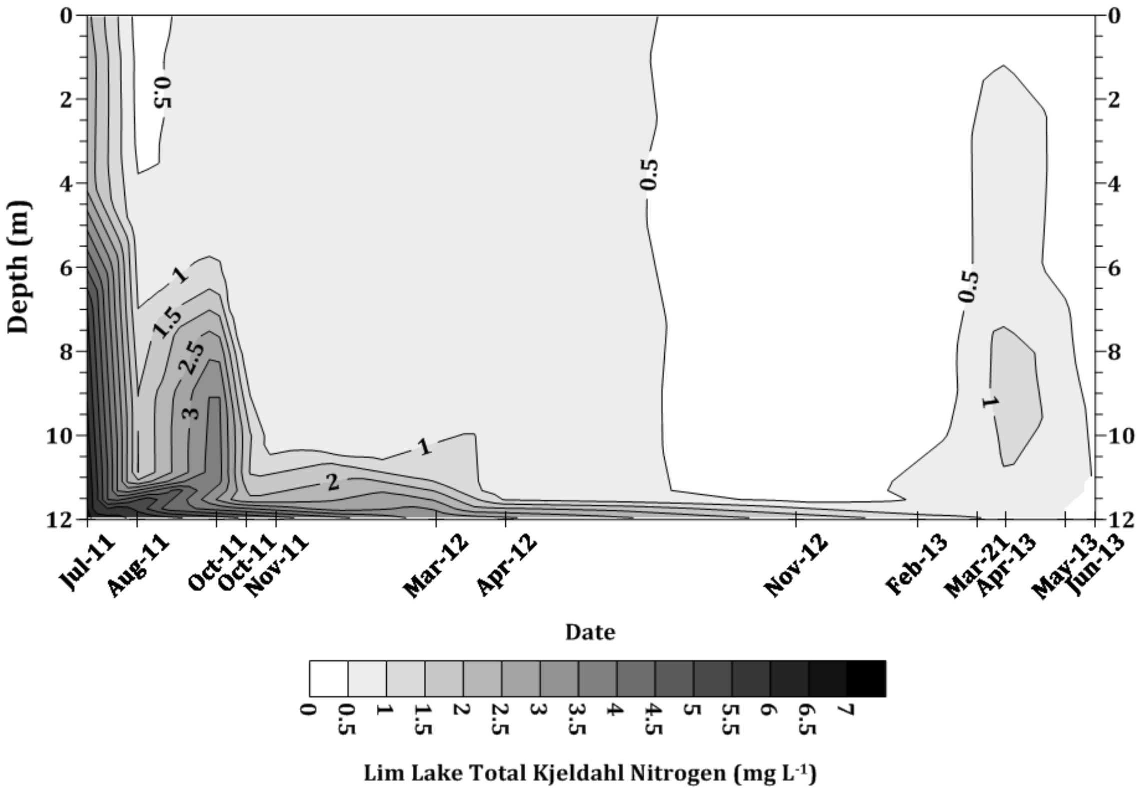


Figure 1.31. Lim Lake total kjeldahl nitogen (mg L^{-1}) profiles from Jul 2011-Jun 2013.

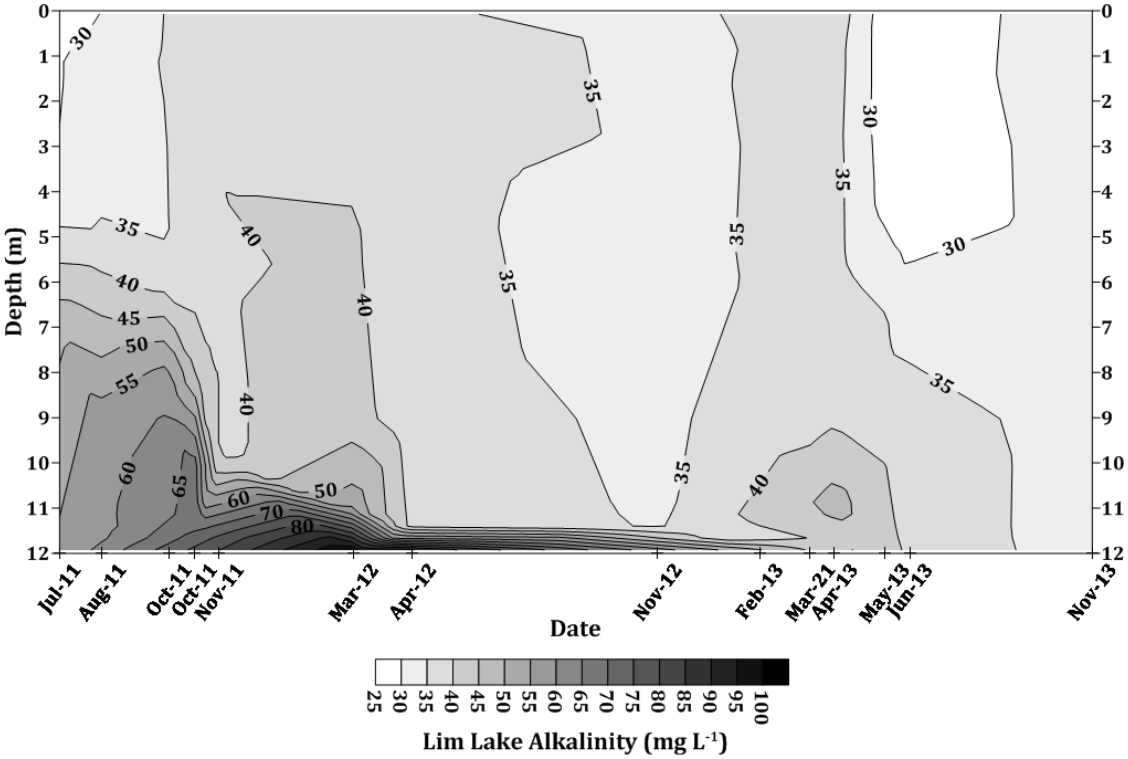


Figure 1.32. Lim Lake alkalinity (mg L^{-1}) profiles from Jul 2011-Nov 2013.

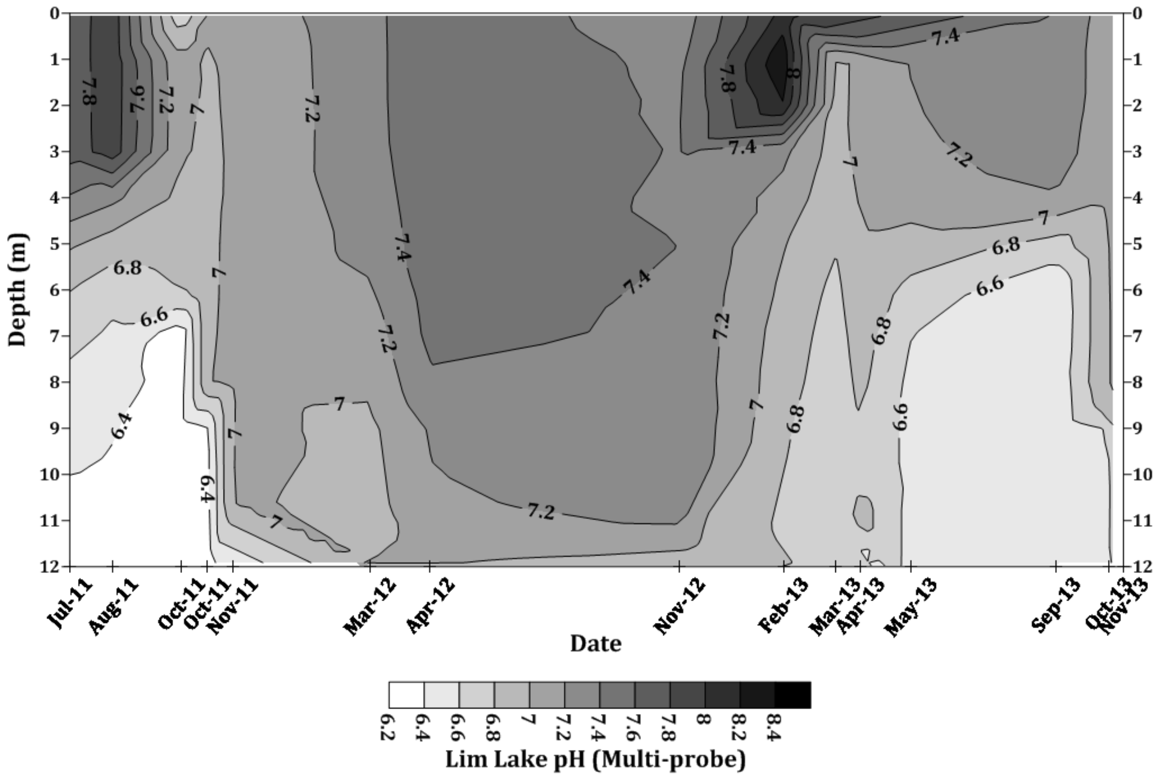


Figure 1.33. Lim Lake pH multi-probe profiles from Jul 2011-Nov 2013.

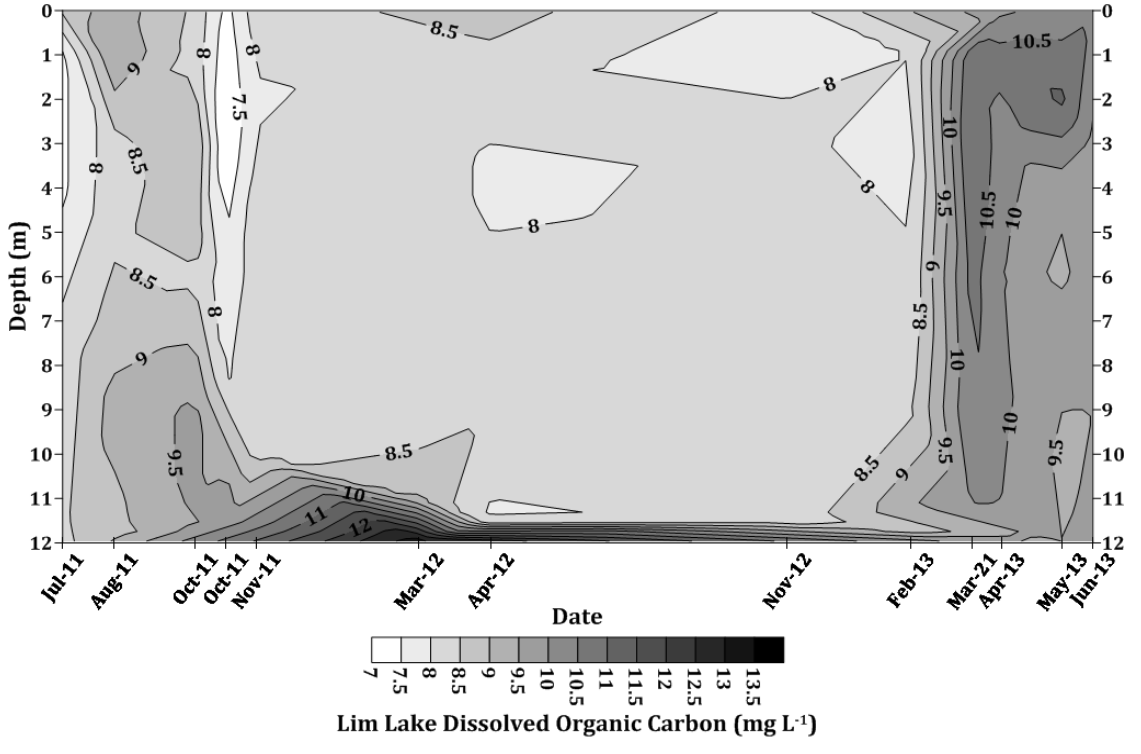


Figure 1.34. Lim Lake dissolved organic carbon (mg L^{-1}) profiles from Jul 2011-Jun 2013.

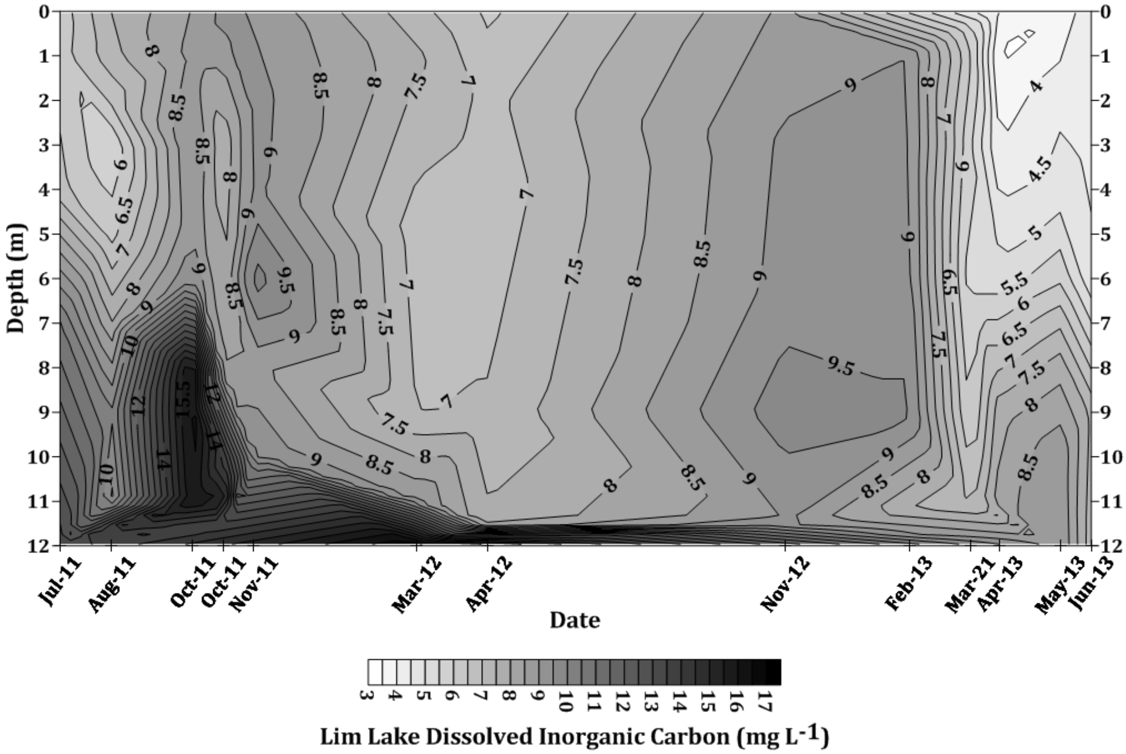


Figure 1.35. Lim Lake dissolved inorganic carbon (mg L^{-1}) profiles from Jul 2011-Jun 2013.

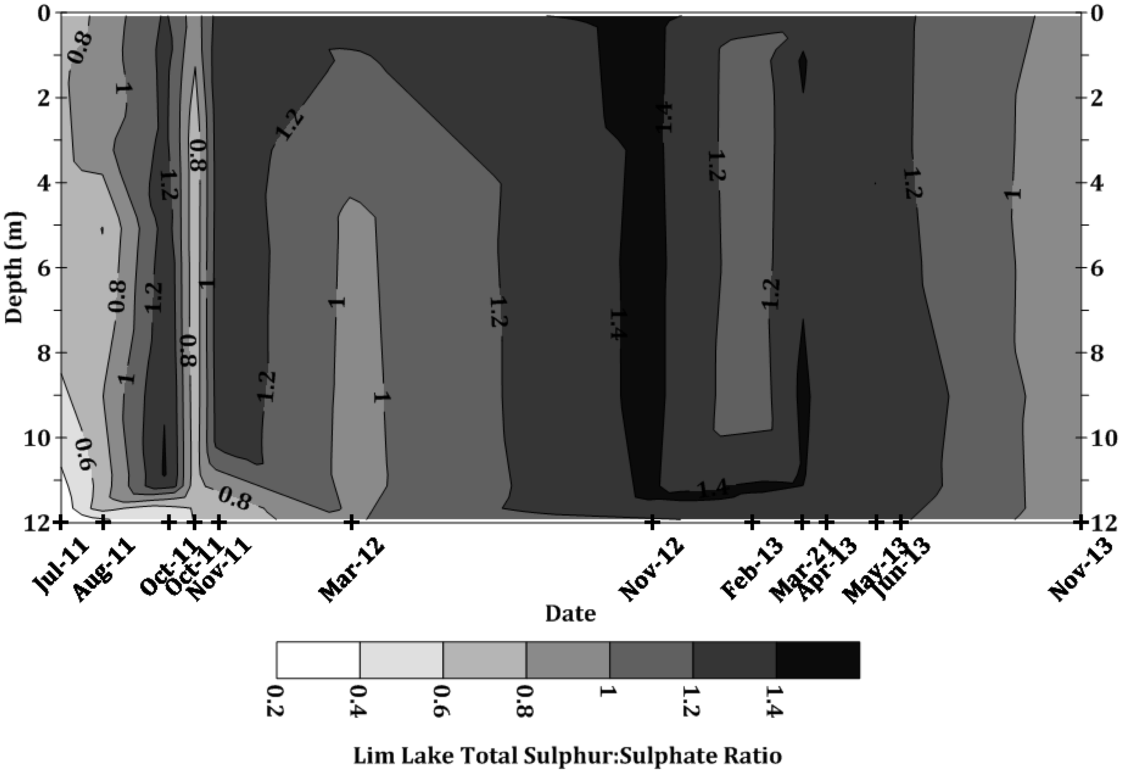


Figure 1.36. Lim Lake total sulphur to sulphate ratio from Jul 2011-Nov 2013.

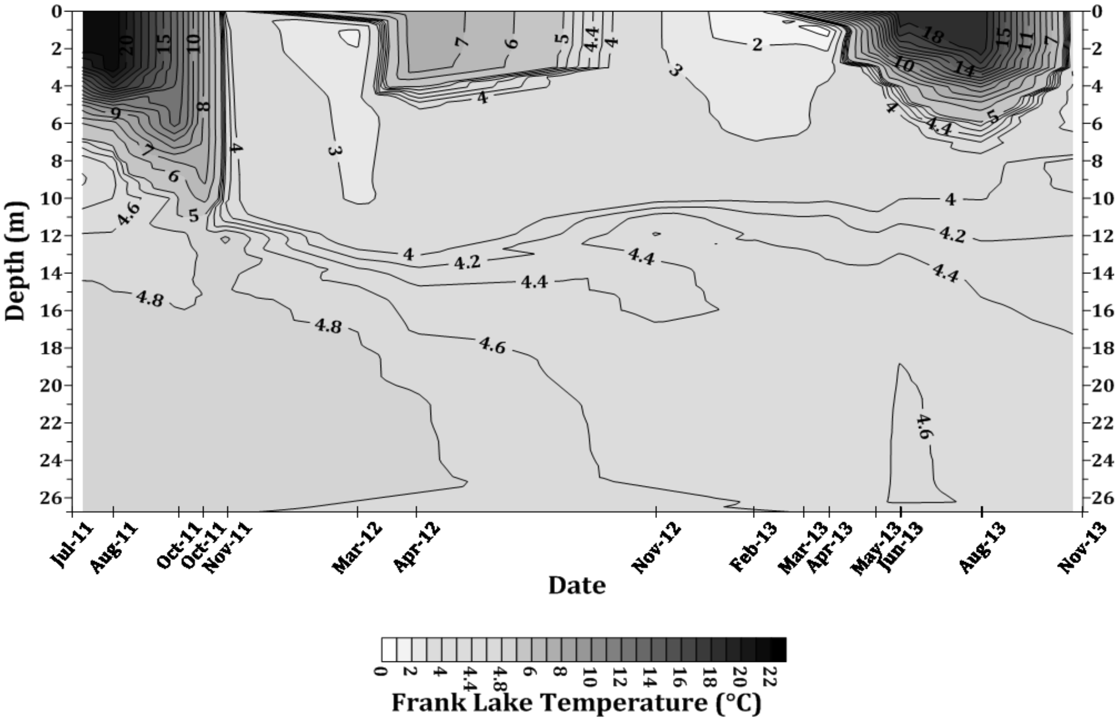


Figure 1.37. Frank Lake temperature (°C) profiles from Jul 2011-Nov 2013. Note variable contour gradients in legend between 3°C and 4°C to demonstrate dichothermy.

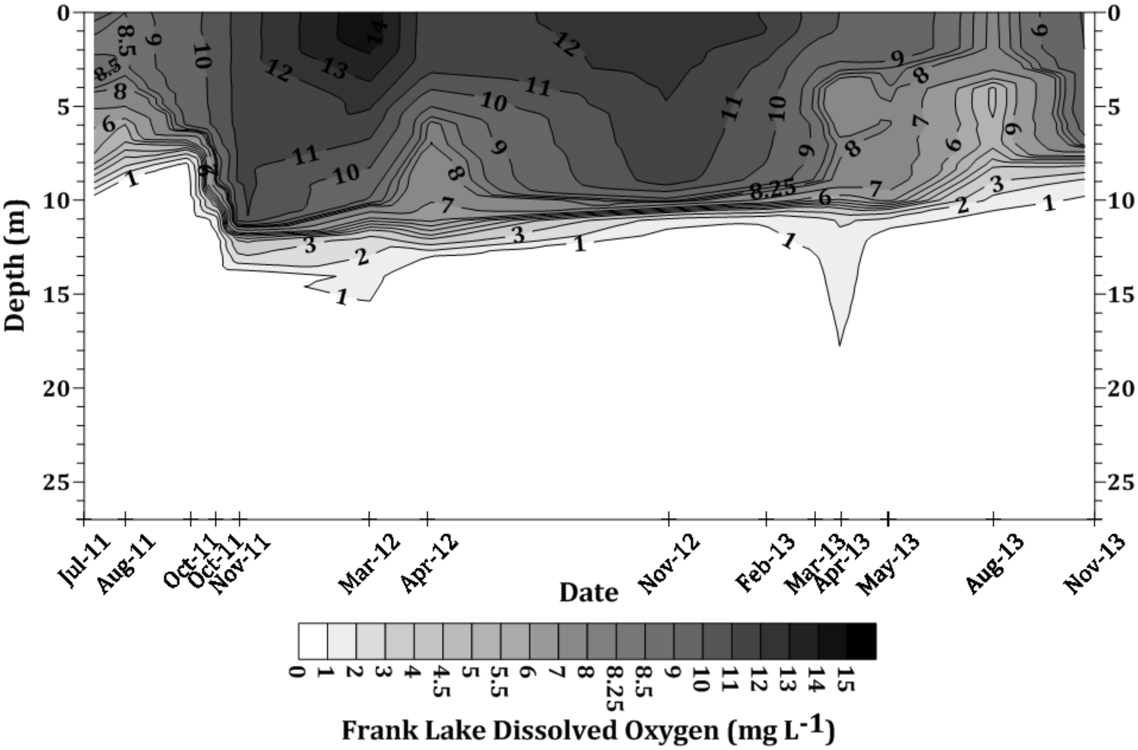


Figure 1.38. Frank Lake dissolved oxygen (mg L^{-1}) profiles from Jul 2011-Nov 2013. Note variable contour gradients in legend between 4-6mg L^{-1} and 8-8.5mg L^{-1} to demonstrate negative heterograde trends.

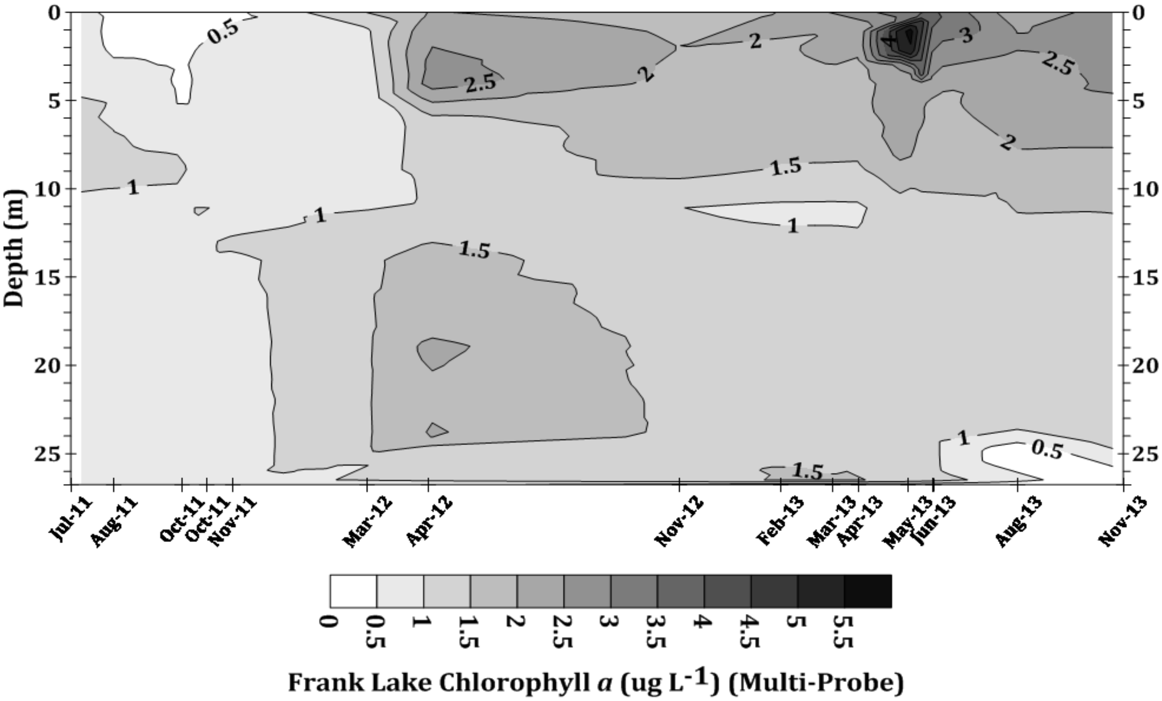


Figure 1.39. Frank Lake chlorophyll a (μg L-1) multi-probe profiles from Jul 2011-Nov 2013.

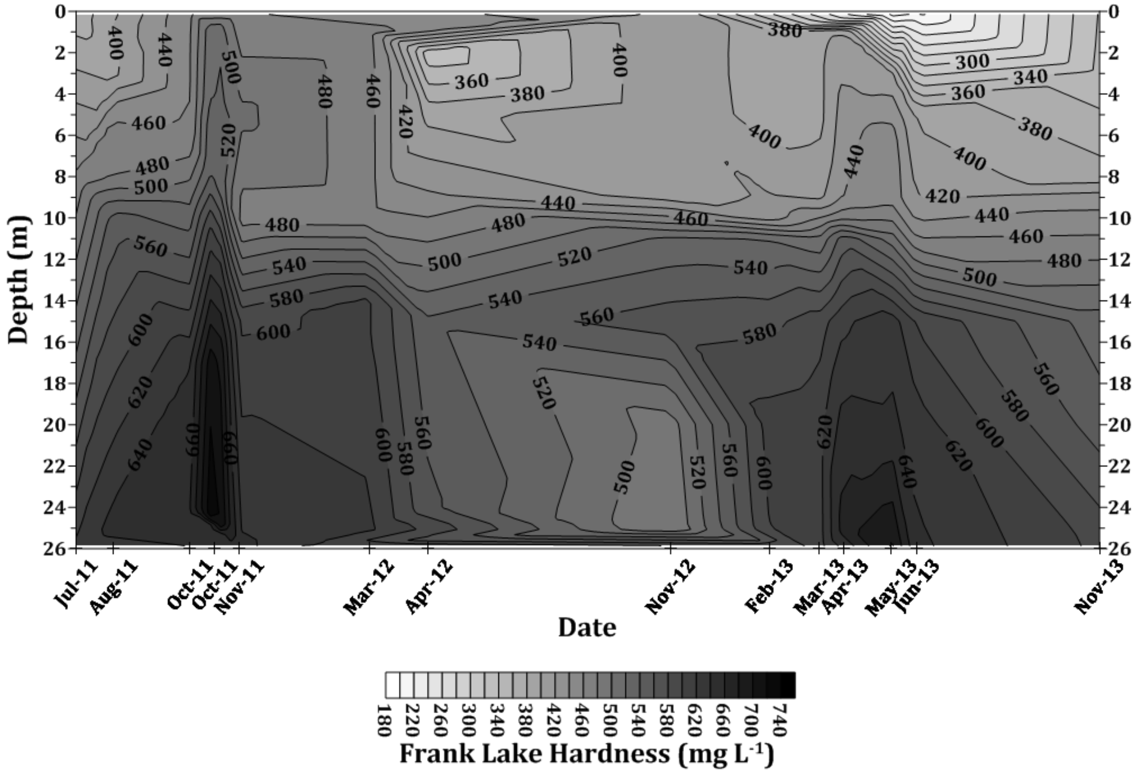


Figure 1.40. Frank Lake hardness (mg L-1) profile calculcations from Jul 2011-Nov 2013.

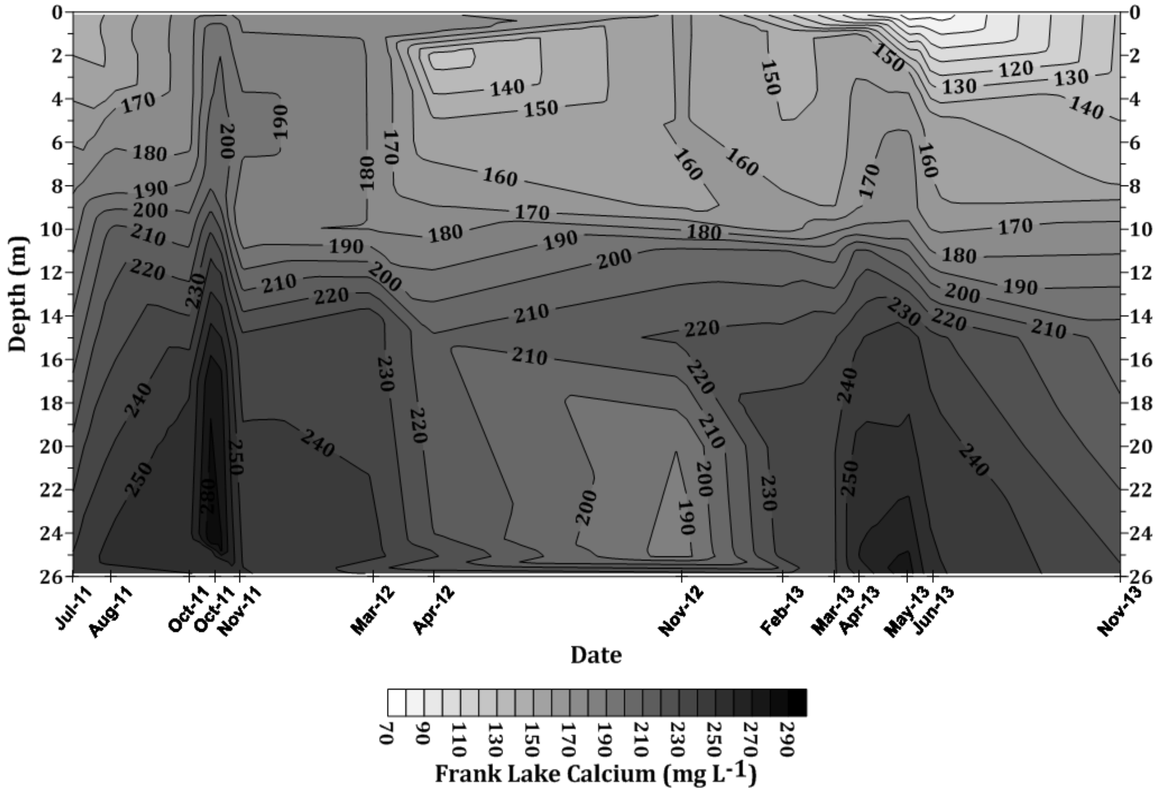


Figure 1.41. Frank Lakecalcium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

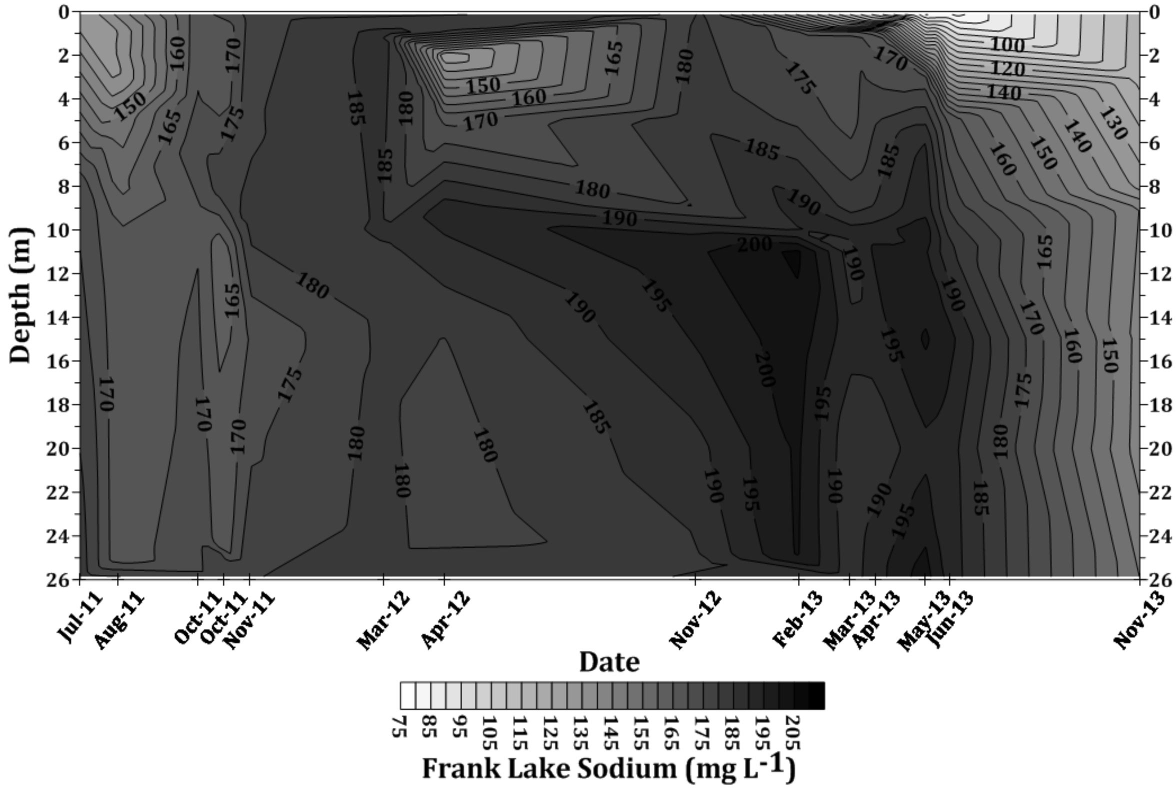


Figure 1.42. Frank Lake sodium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

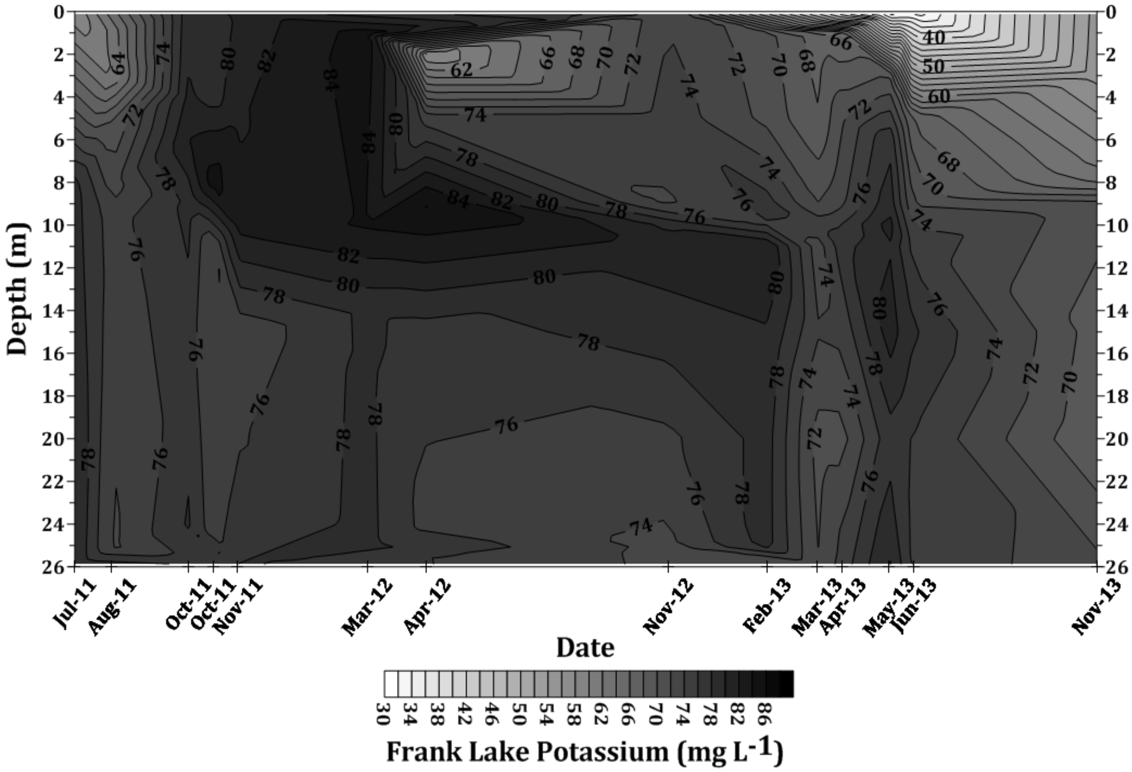


Figure 1.43. Frank Lake potassium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

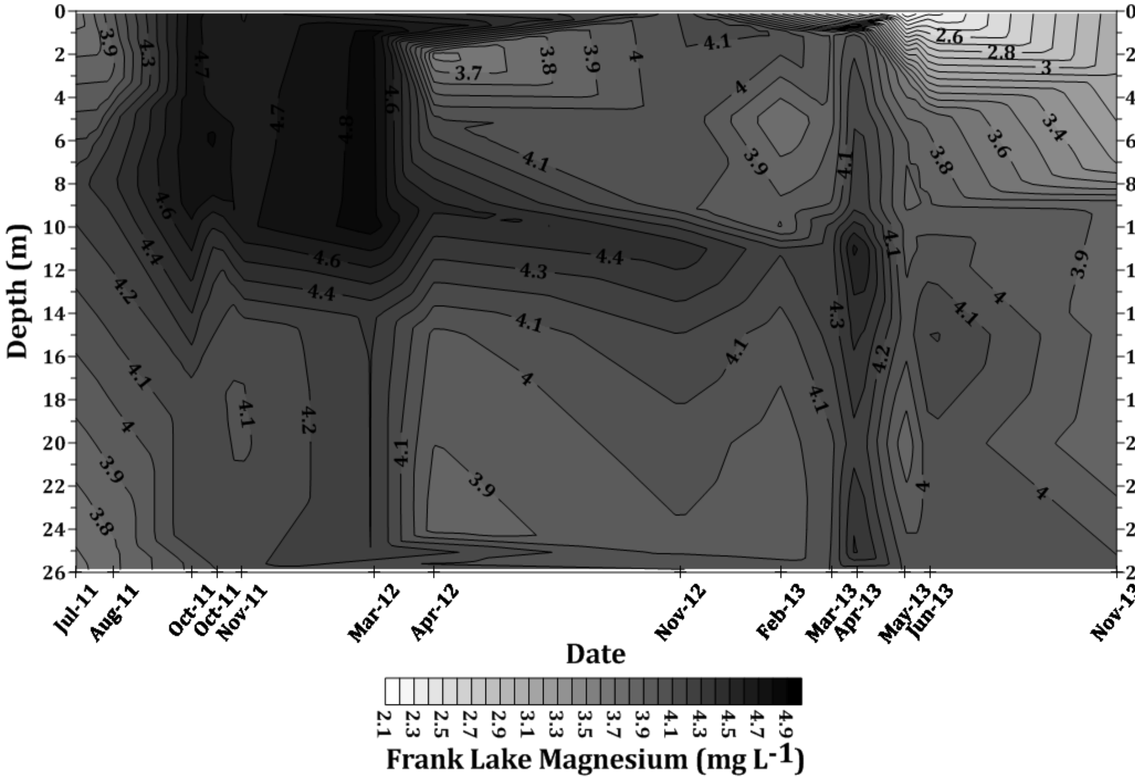


Figure 1.44. Frank Lake magnesium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

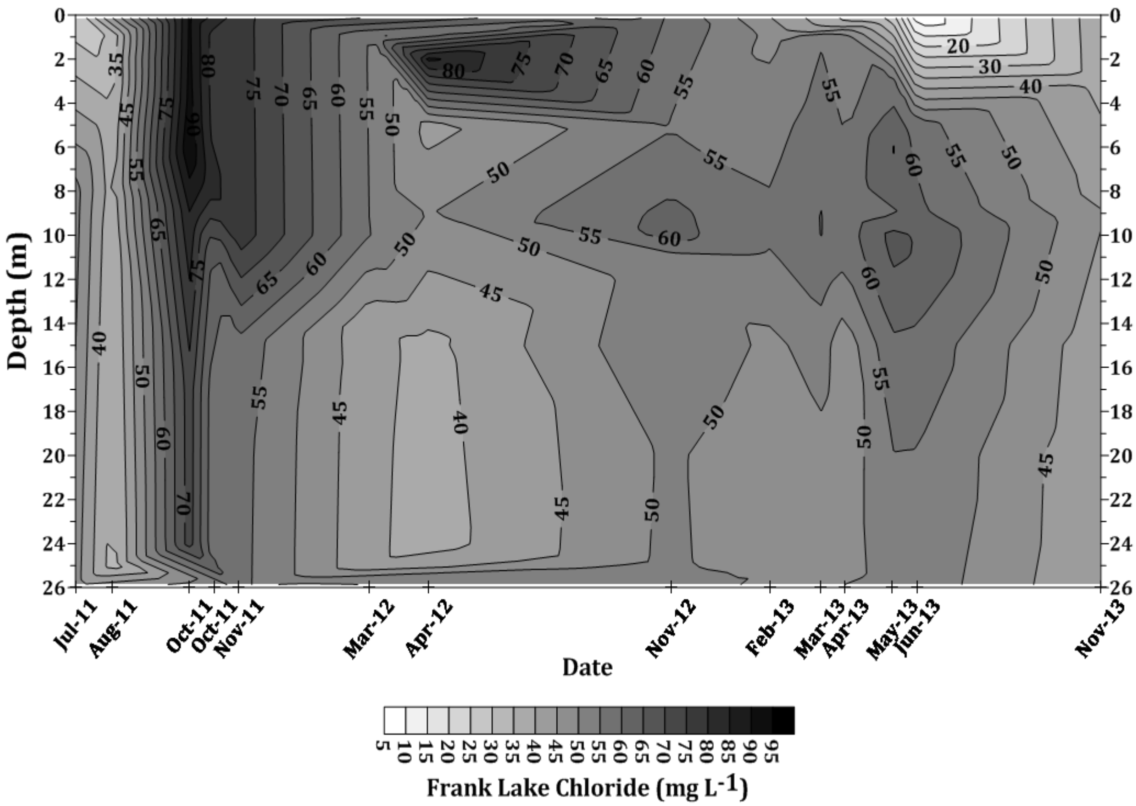


Figure 1.45. Frank Lake chloride (mg L^{-1}) profiles from Jul 2011-Nov 2013.

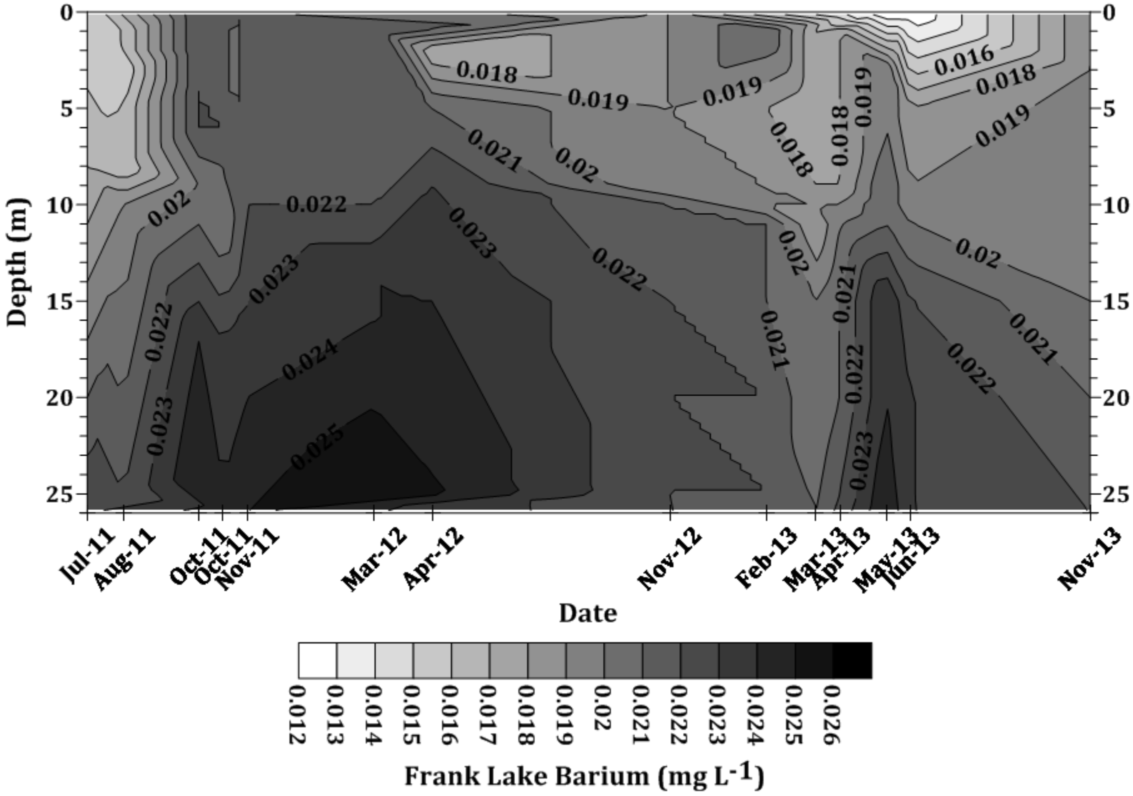


Figure 1.46. Lim Lake barium(mg L^{-1}) profiles from Jul 2011-Nov 2013.

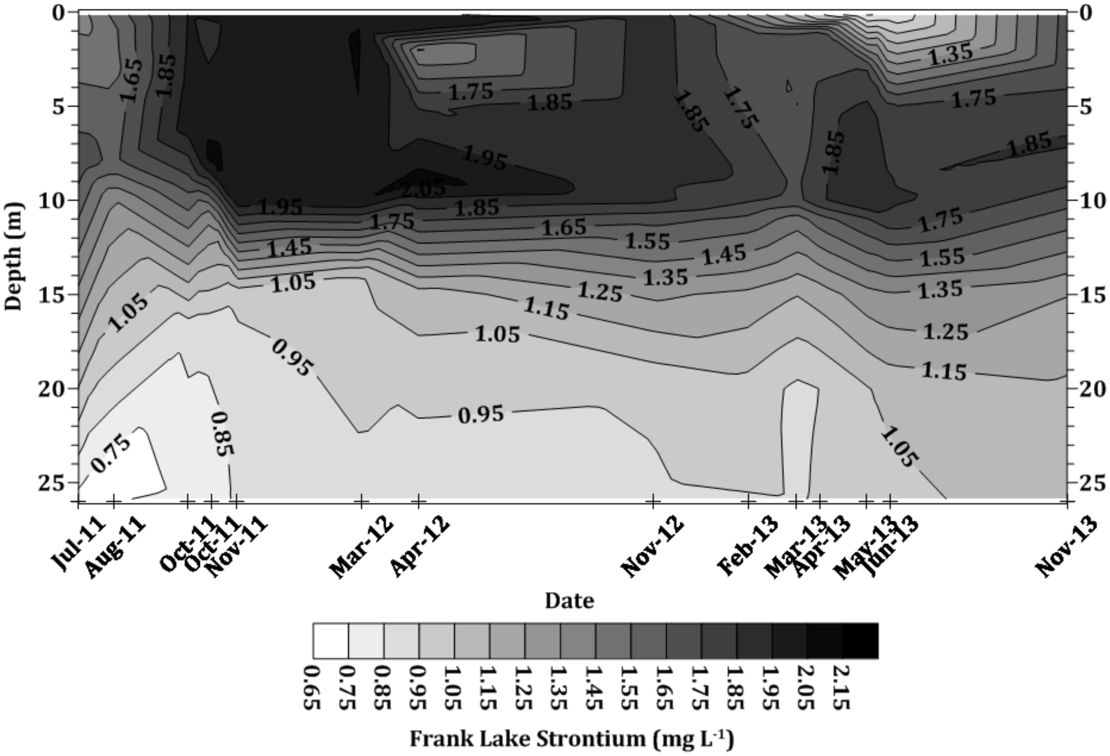


Figure 1.47. Frank Lake strontium (mg L^{-1}) profiles from Jul 2011-Nov 2013.

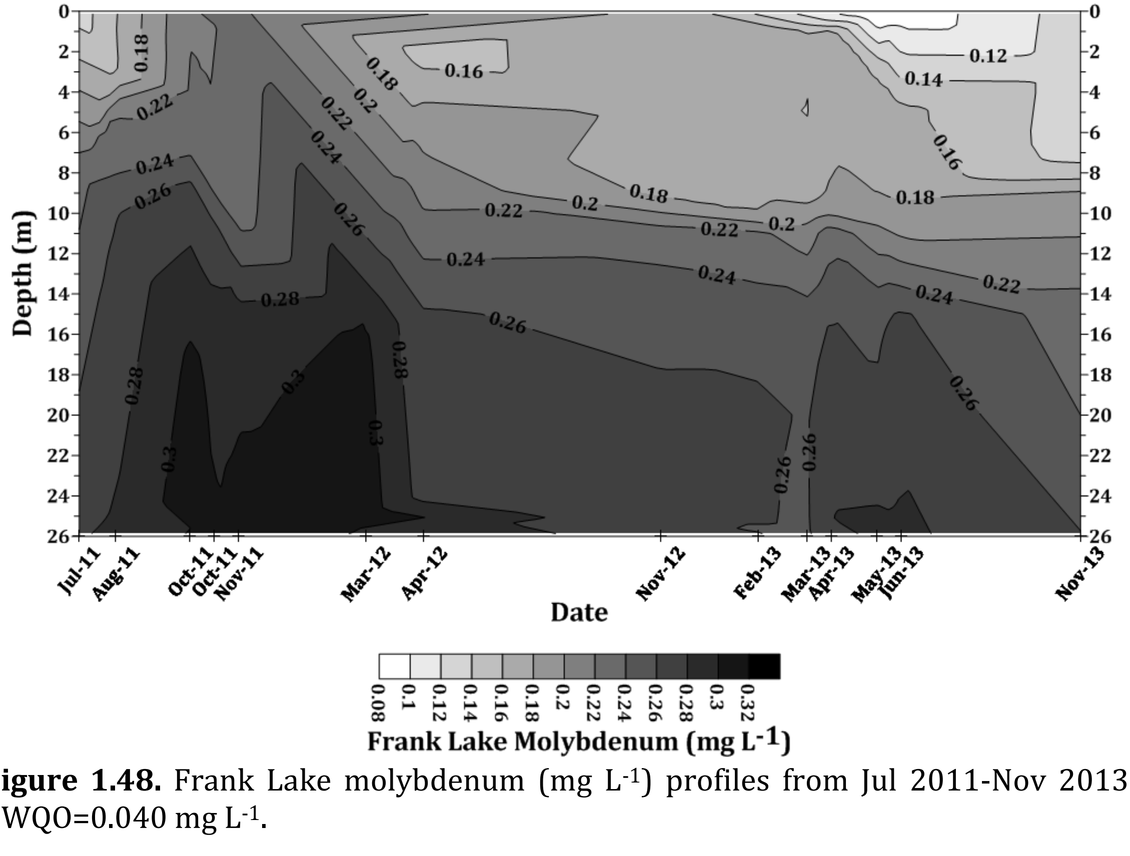


Figure 1.48. Frank Lake molybdenum (mg L^{-1}) profiles from Jul 2011-Nov 2013. PWQO=0.040 mg L^{-1}.

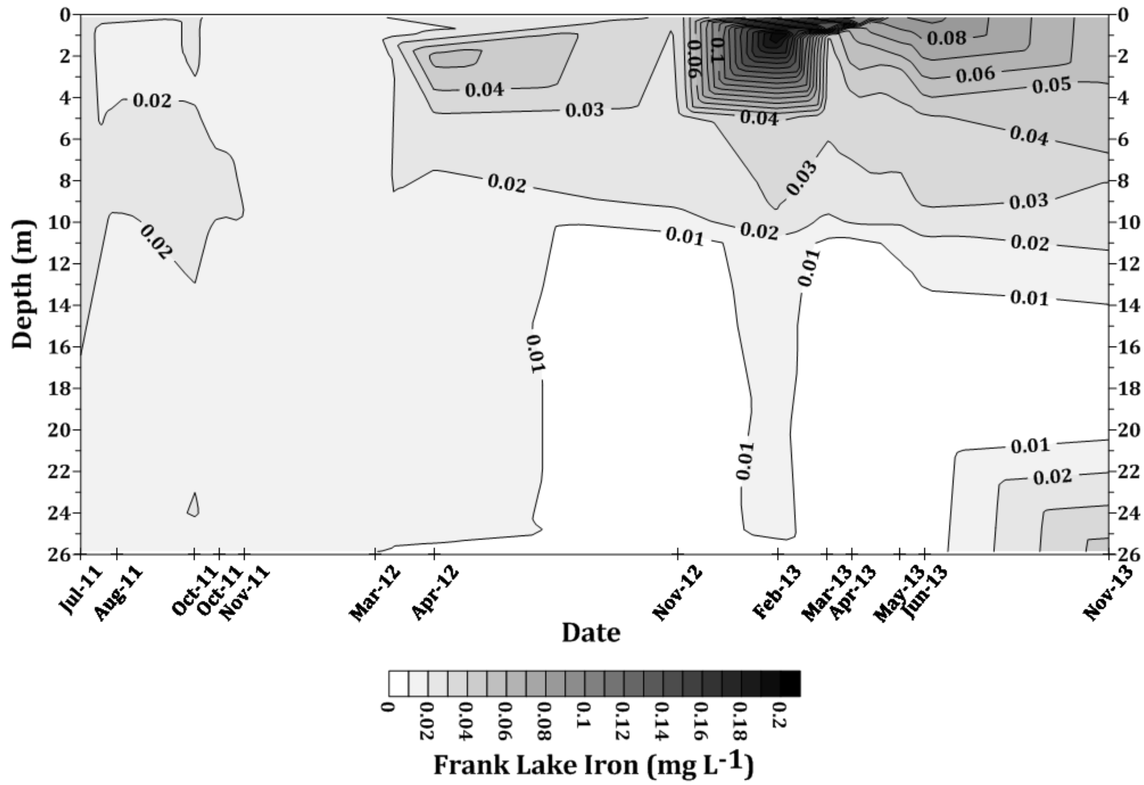


Figure 1.49. Frank Lake iron (mg L^{-1}) profiles from Jul 2011-Nov 2013.

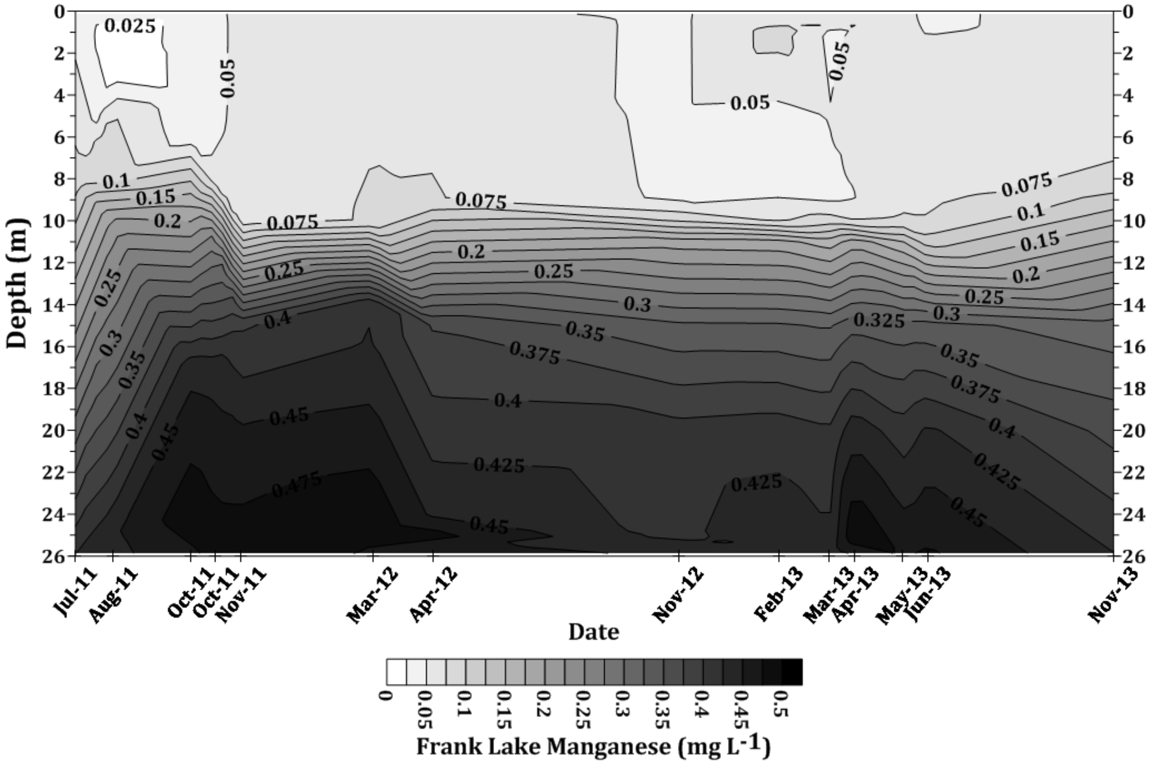


Figure 1.50. Frank Lake manganese (mg L^{-1}) profiles from Jul 2011-Nov 2013.

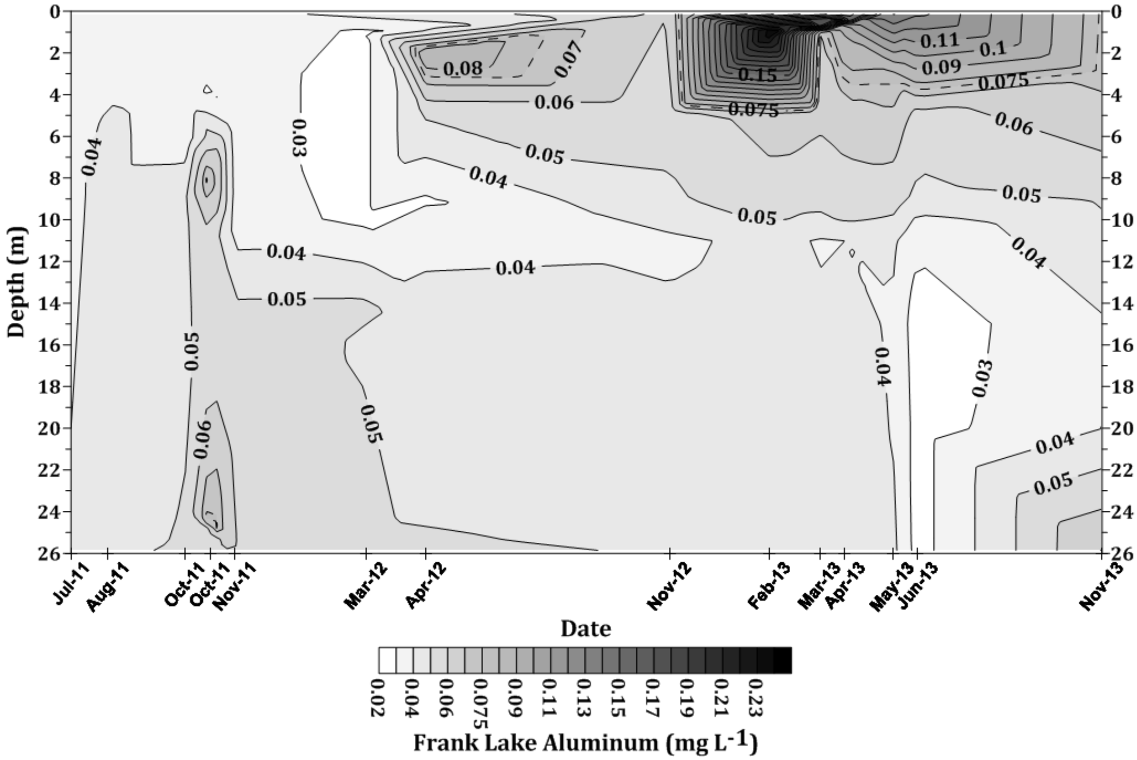


Figure 1.51. Frank Lake aluminum (mg L^{-1}) profiles from Jul 2011-Nov 2013. Dashed contour = PWQO (0.075 mg L^{-1}).

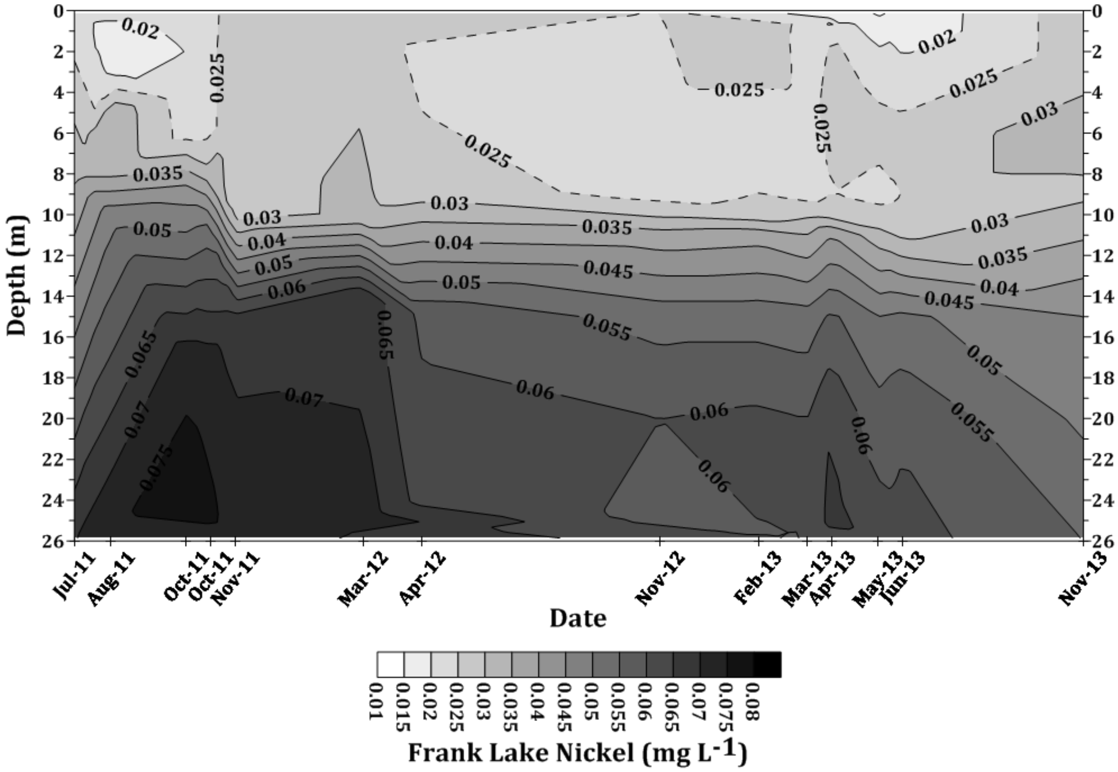


Figure 1.52. Frank Lake nickel (mg L^{-1}) profiles from Jul 2011-Nov 2013. Dashed contour=PWQO (0.025 mg L^{-1}).

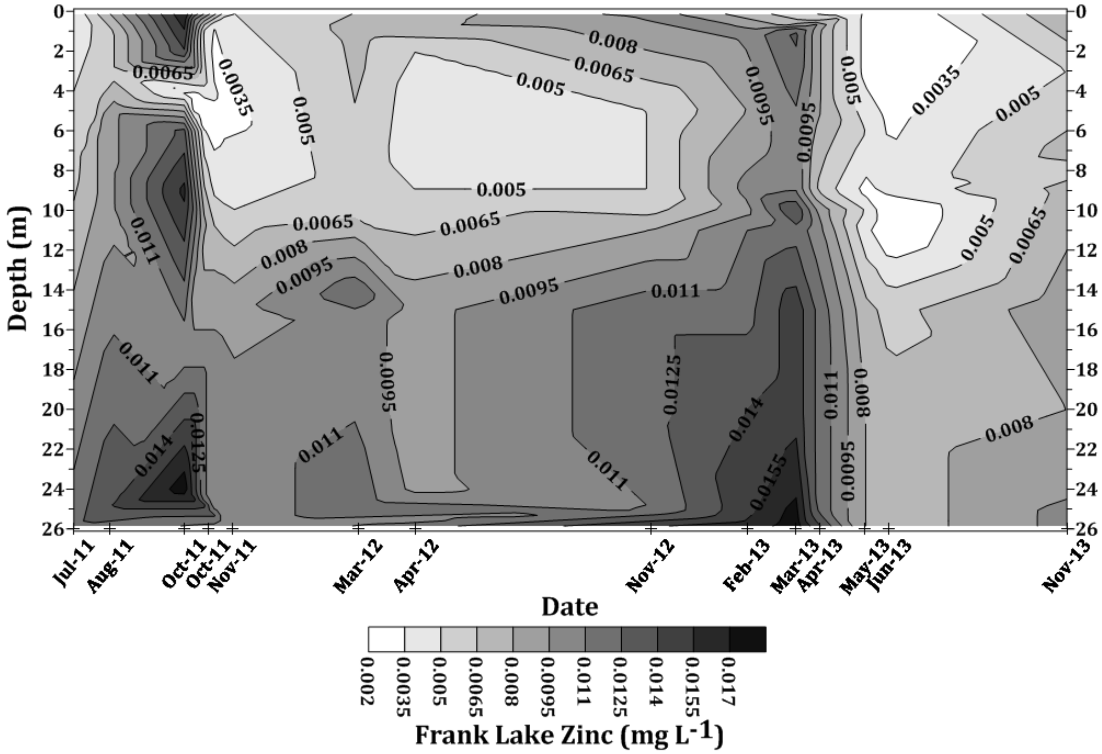


Figure 1.53. Frank Lake zinc (mg L^{-1}) profiles from Jul 2011-Nov 2013.

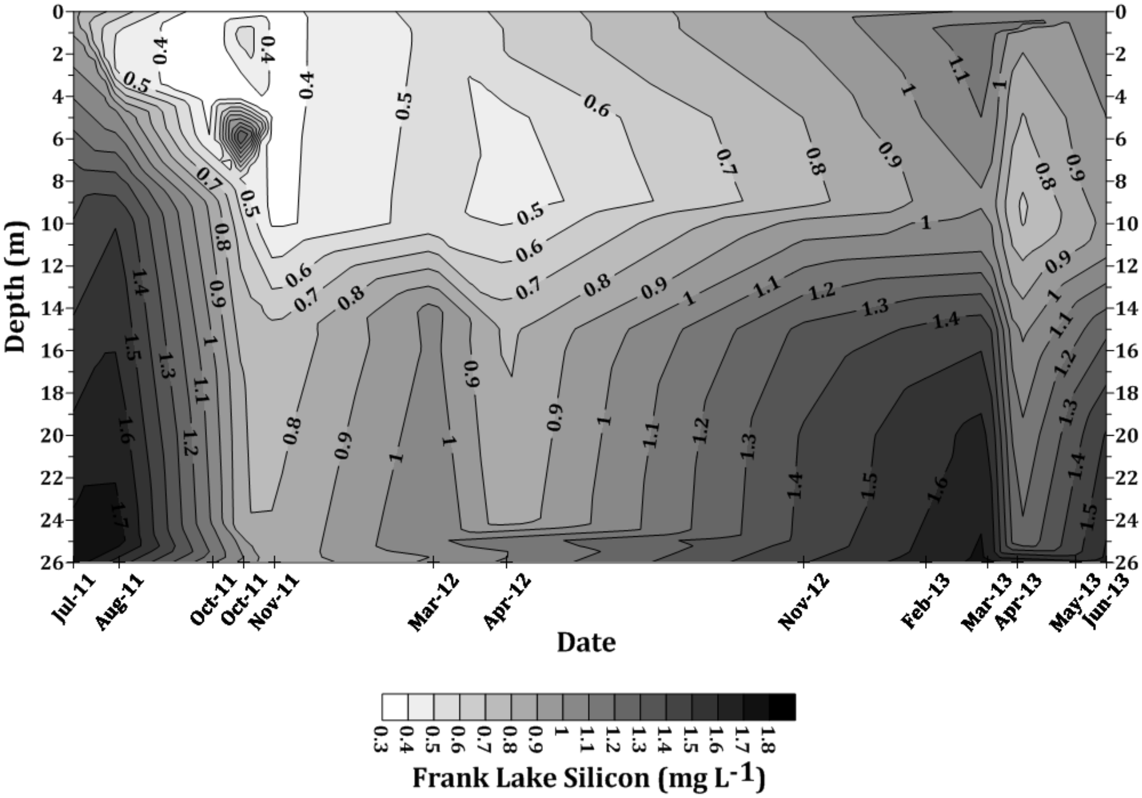


Figure 1.54. Frank Lake silicon (mg L^{-1}) profiles from Jul 2011-Jun 2013.

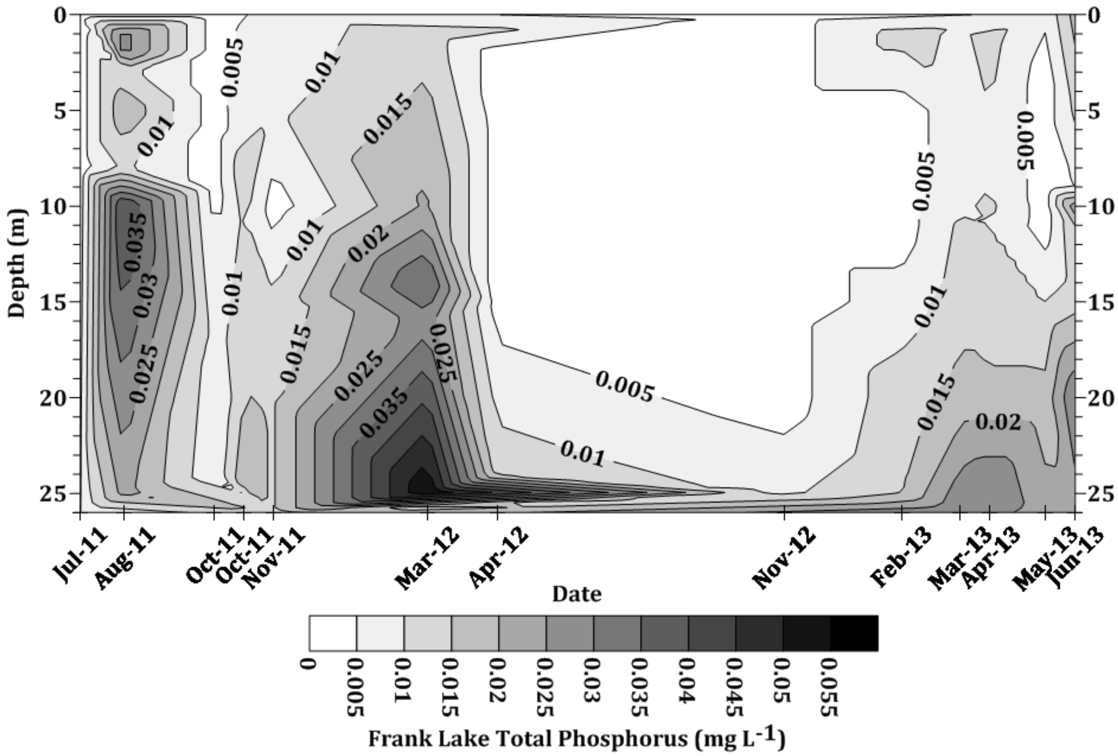


Figure 1.55. Frank Lake total phosphorus (mg L^{-1}) profiles from Jul 2011-Nov 2013.

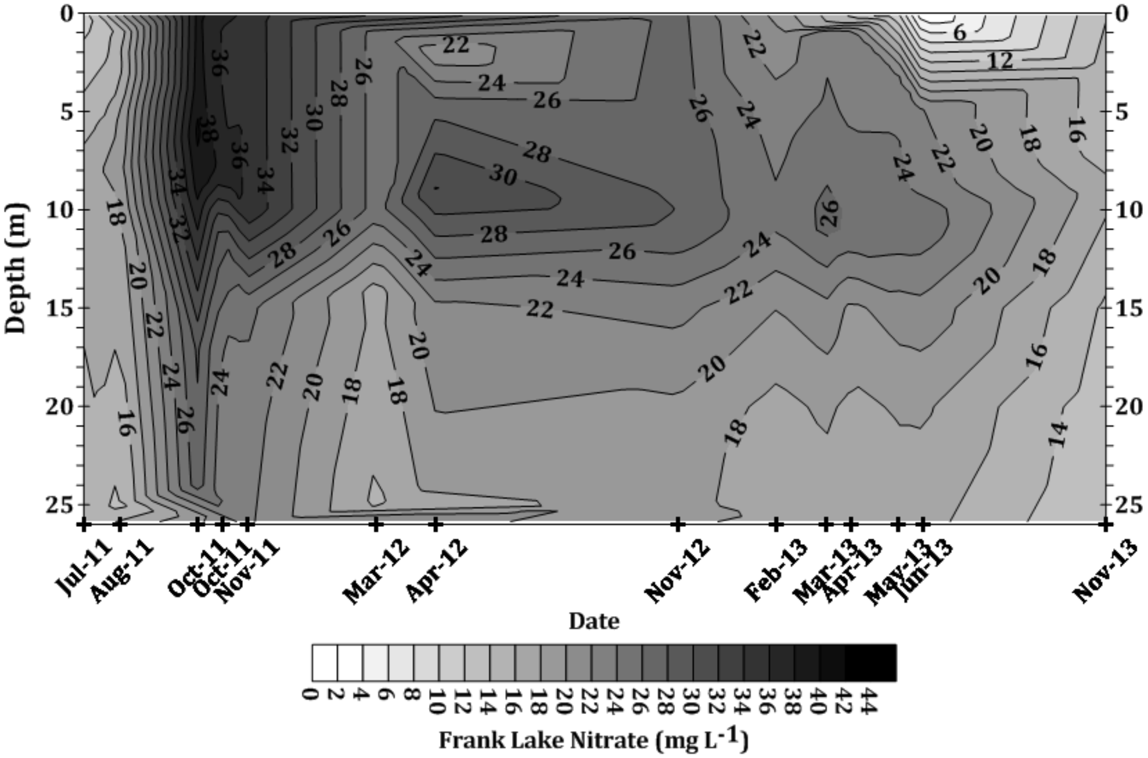


Figure 1.56. Frank Lake nitrate (mg L^{-1}) from Jul 2011-Nov 2013.

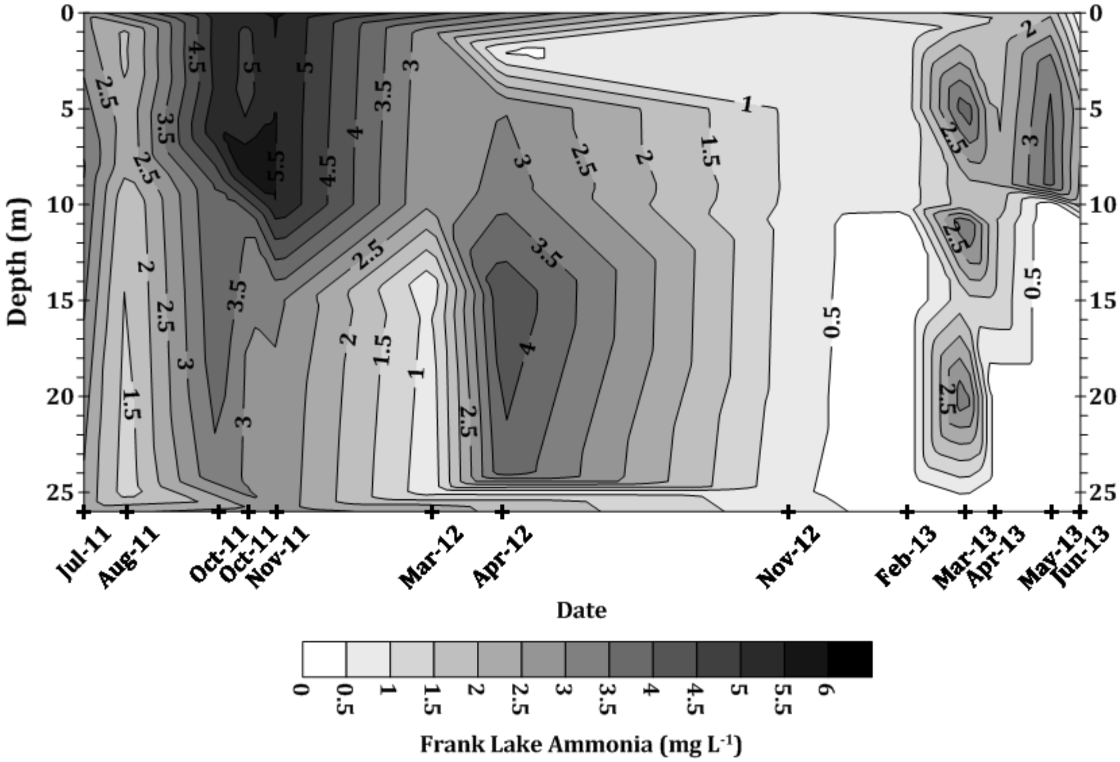


Figure 1.57. Frank Lake ammonia (mg L^{-1}) from Jul 2011-Jun 2013.

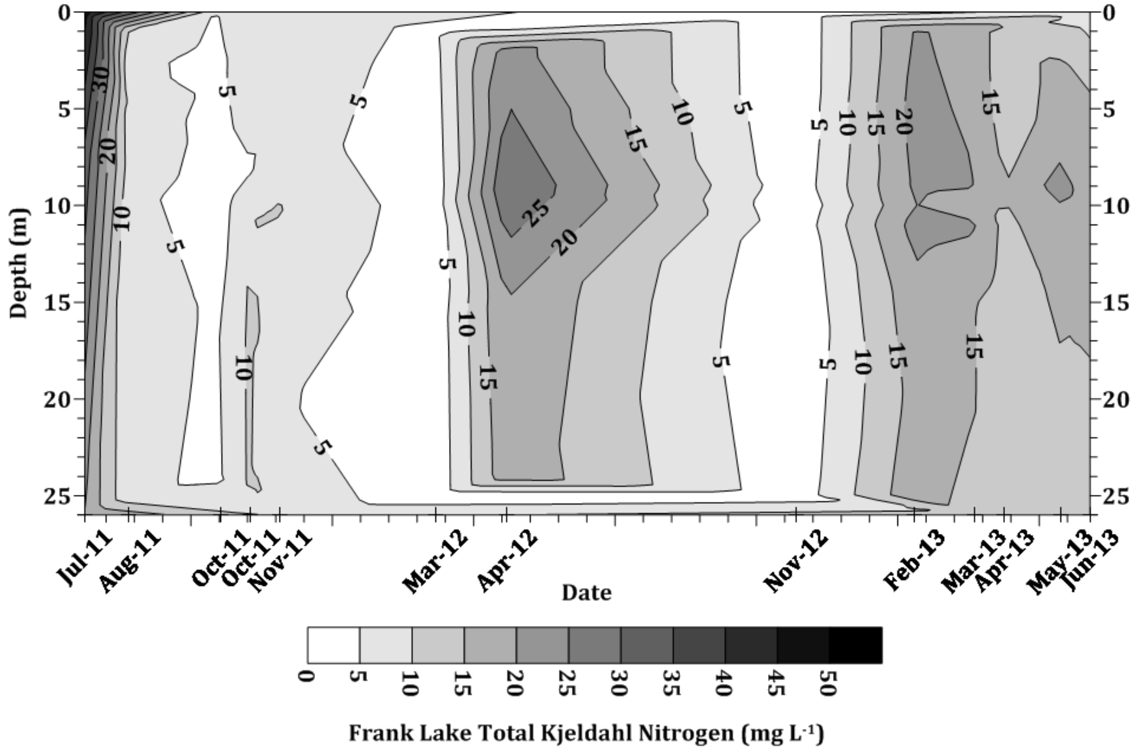


Figure 1.58. Frank Lake total kjeldahl nitrogen (mg L^{-1}) from Jul 2011-Nov 2013.

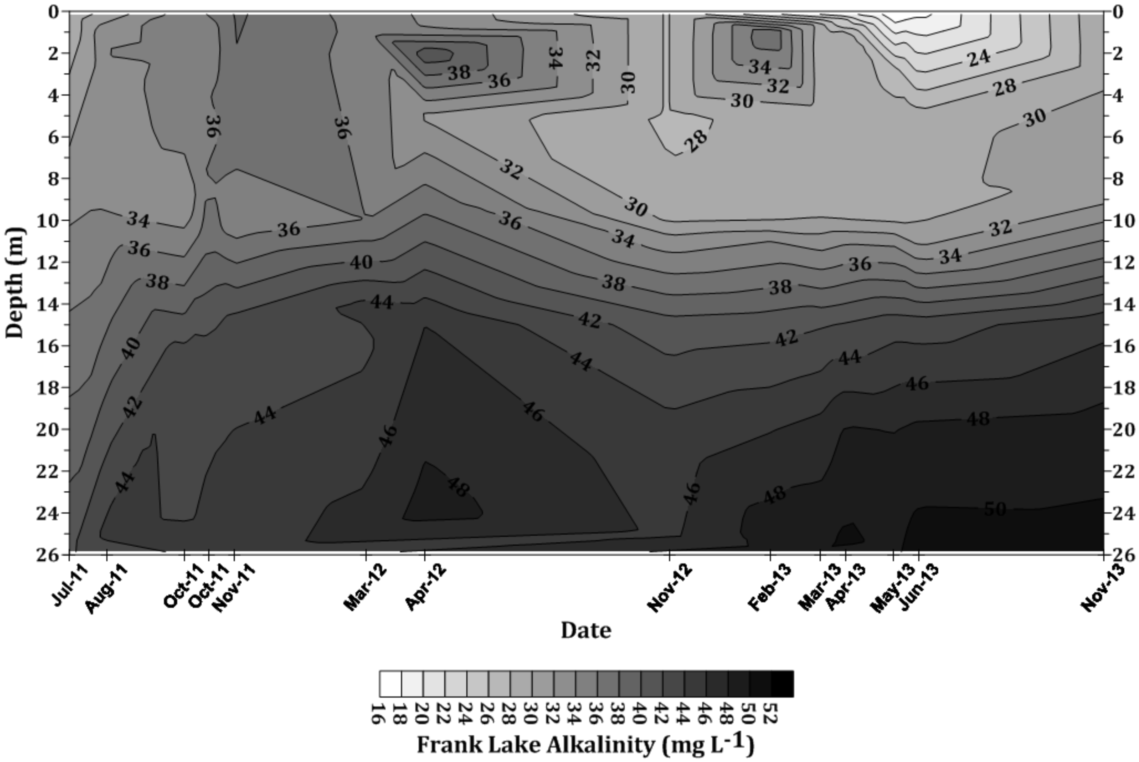


Figure 1.59. Frank Lake alkalinity (mg L^{-1}) profiles from Jul 2011-Nov 2013.

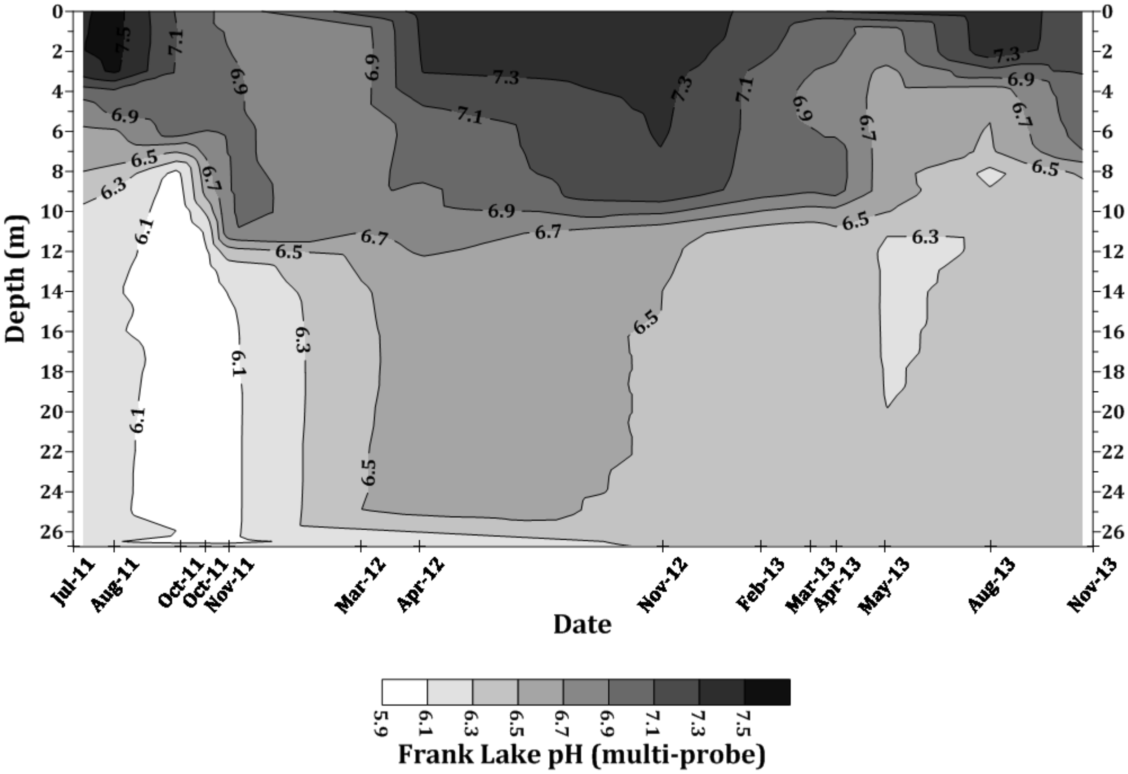


Figure 1.60. Frank Lake pH multi-probe profiles from Jul 2011-Nov 2013.

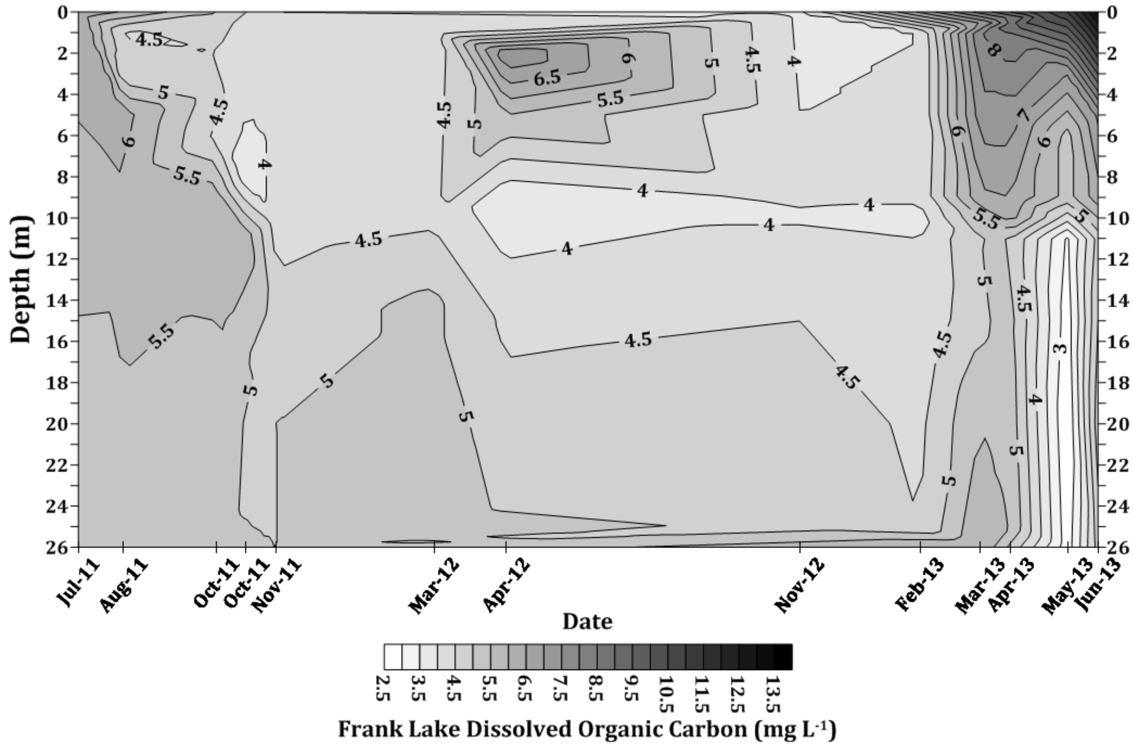


Figure 1.61. Frank Lake DOC (mg L^{-1}) profiles from Jul 2011-Jun 2013.

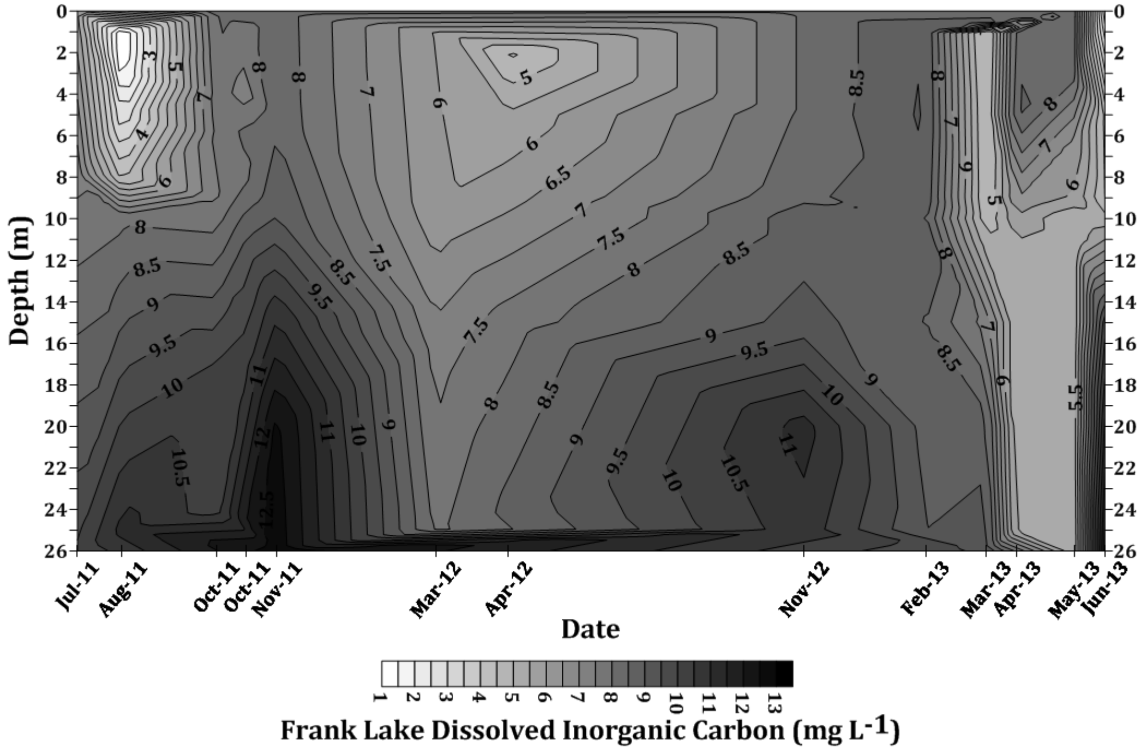


Figure 1.62. Frank Lake DIC (mg L^{-1}) profiles from Jul 2011-Jun 2013.

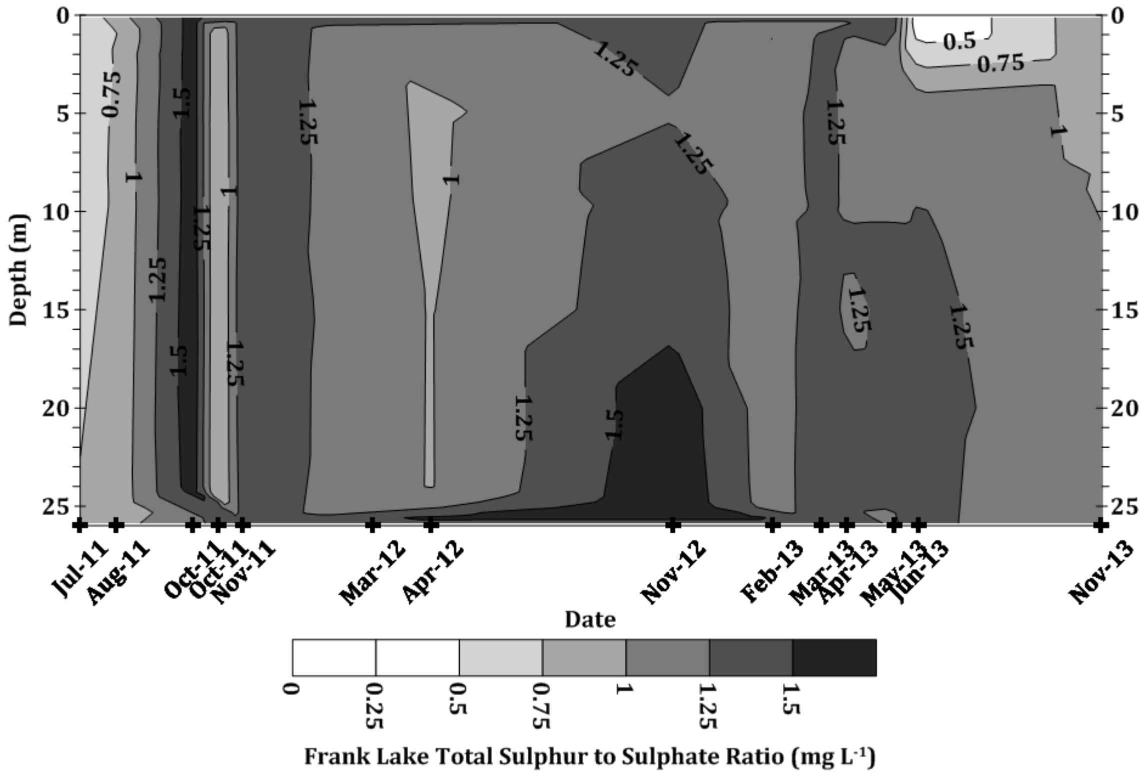


Figure 1.63. Frank Lake total sulphur to sulphate ratio from Jul 2011-Nov 2013.

Figure 1.64. Live *Chaborus flavicans* present in the 11.0m Frank Lake sample during April 2013 (photo taken at Lakehead University).

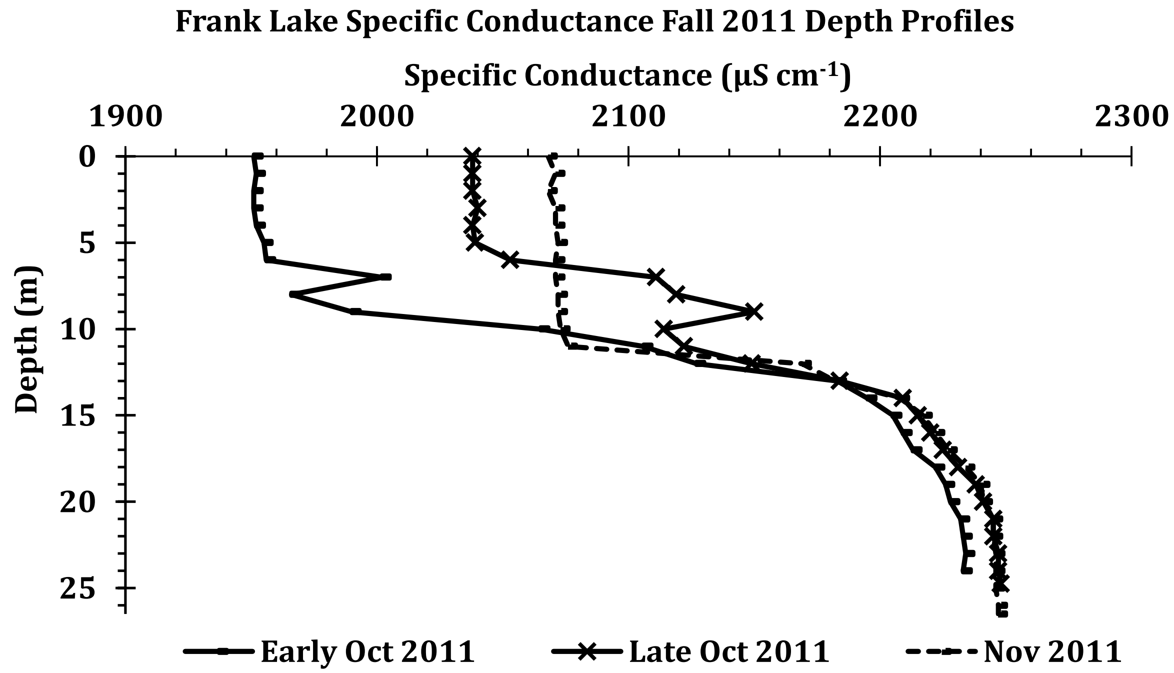


Figure 1.73. Frank Lake specific conductance (μS cm-1) for early and late Oct and Nov 2011, illustrating peaks at 7m and 9m in early and late Oct 2011 respectively.

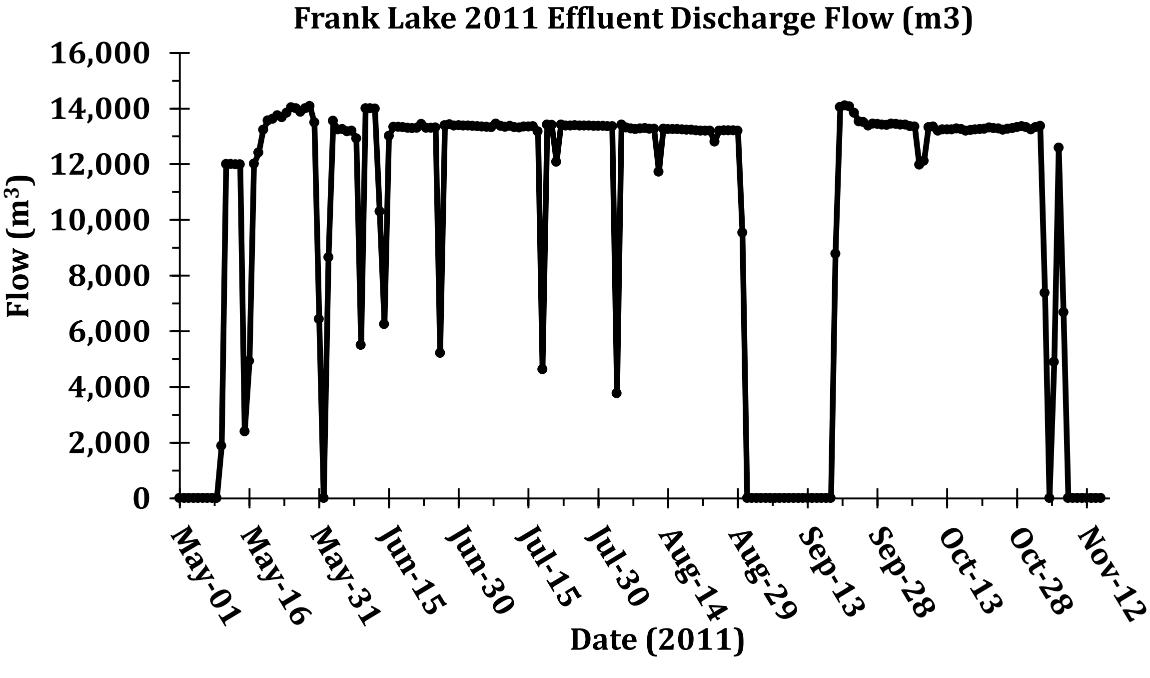


Figure 1.74. Frank Lake effluent discharge flow volume (m^3) from May 2011 - Nov 2011.

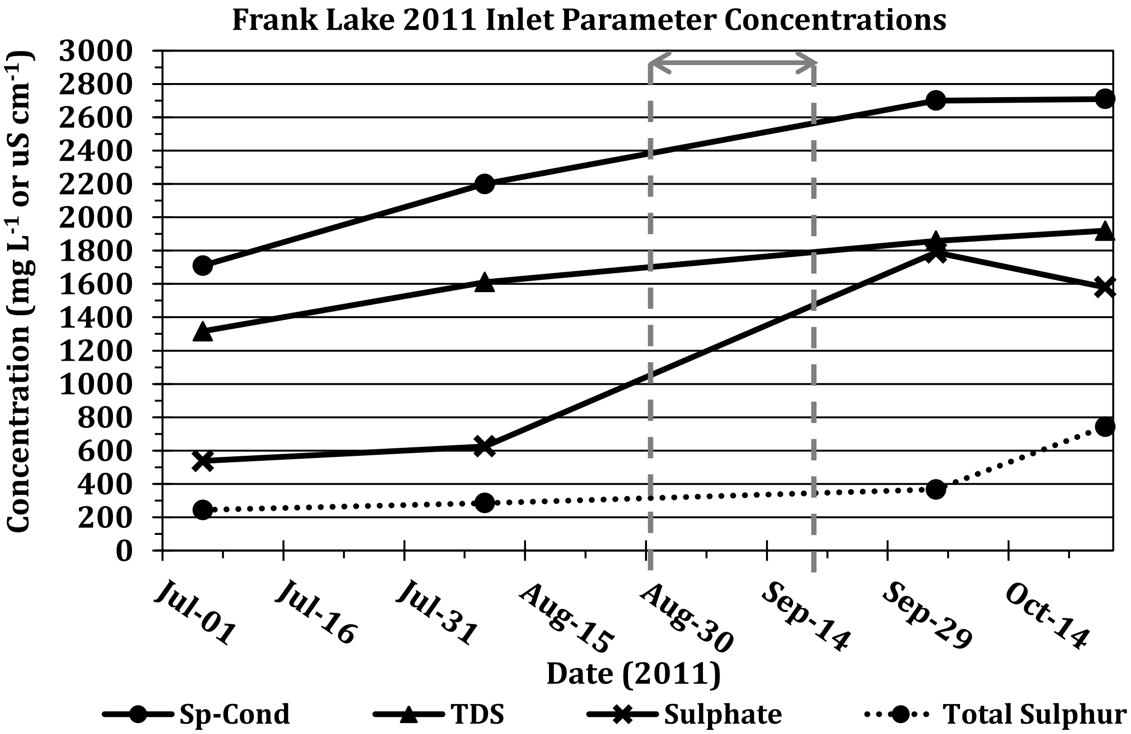


Figure 1.75. Frank Lake effluent discharge specific conductance, TDS, sulphate and total sulphur concentration (mg L^{-1}) and specific conductance (µS cm^{-1}) from Jul 2011 - Oct 2011. Dashed interval indicates absence of effluent discharge.

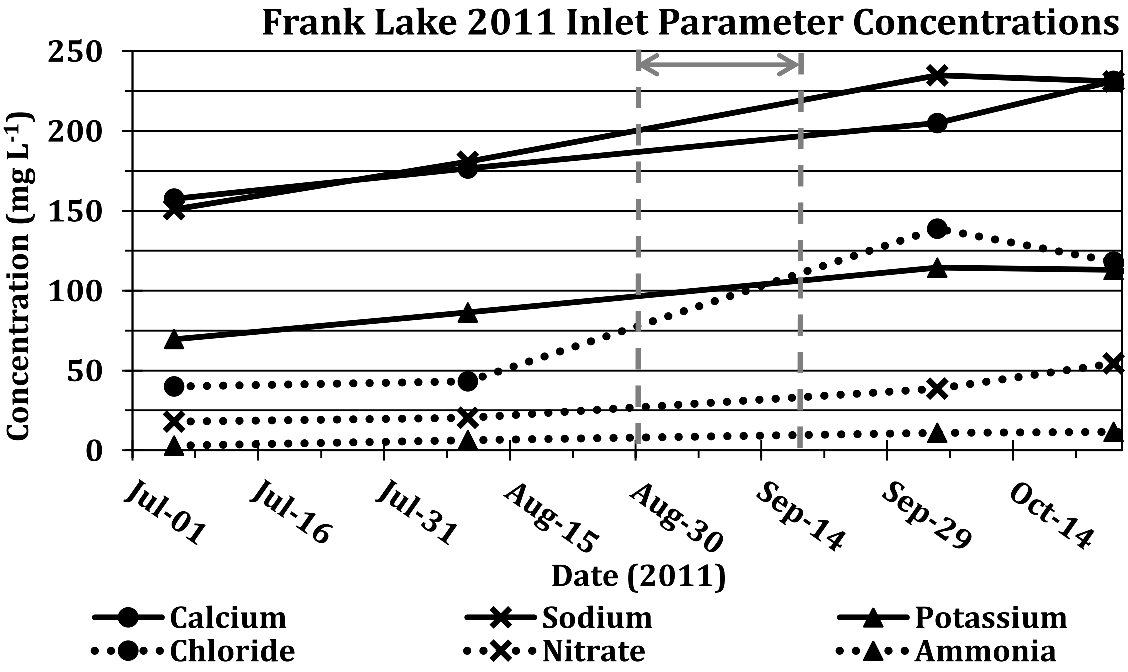


Figure 1.76. Frank Lake 2011 inlet calcium, sodium, potassium, chloride, nitrate and ammonia concentrations (mg L^{-1}). Dashed interval indicates absence of effluent discharge.

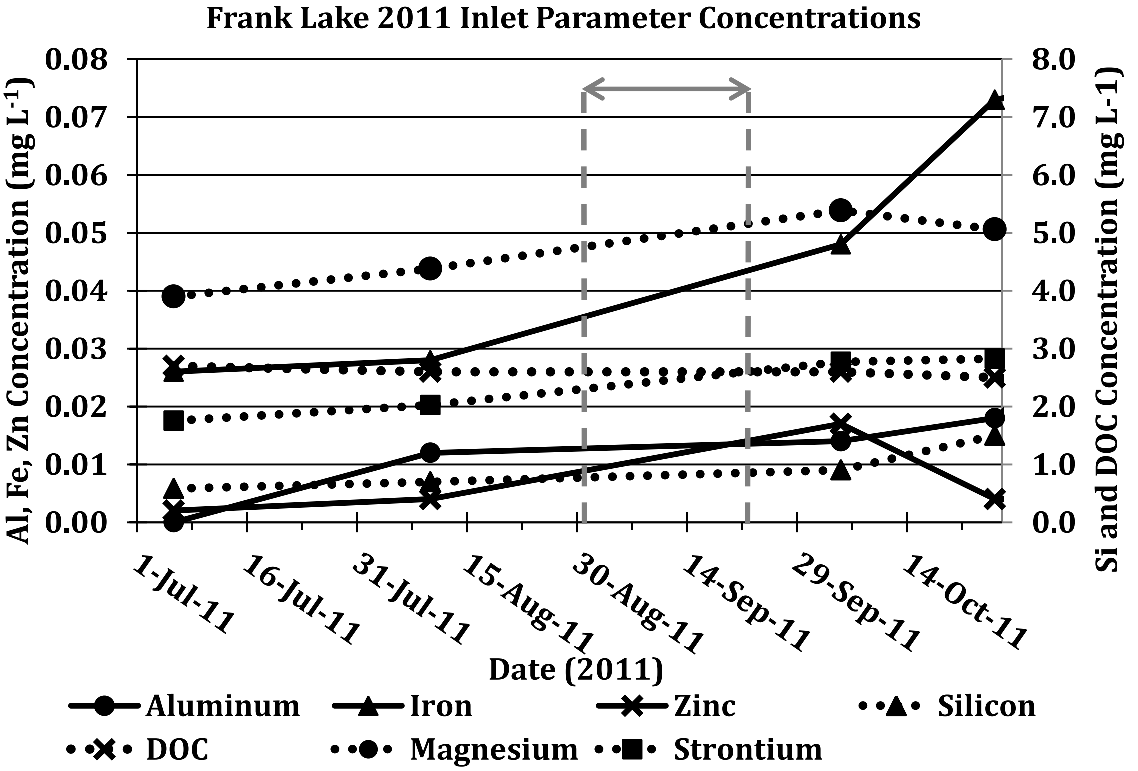


Figure 1.77. Frank Lake 2011 inlet aluminum, iron, zinc, silicon, DOC, magnesium and strontium concentrations (mg L^{-1}). Dashed interval indicates absence of effluent discharge.

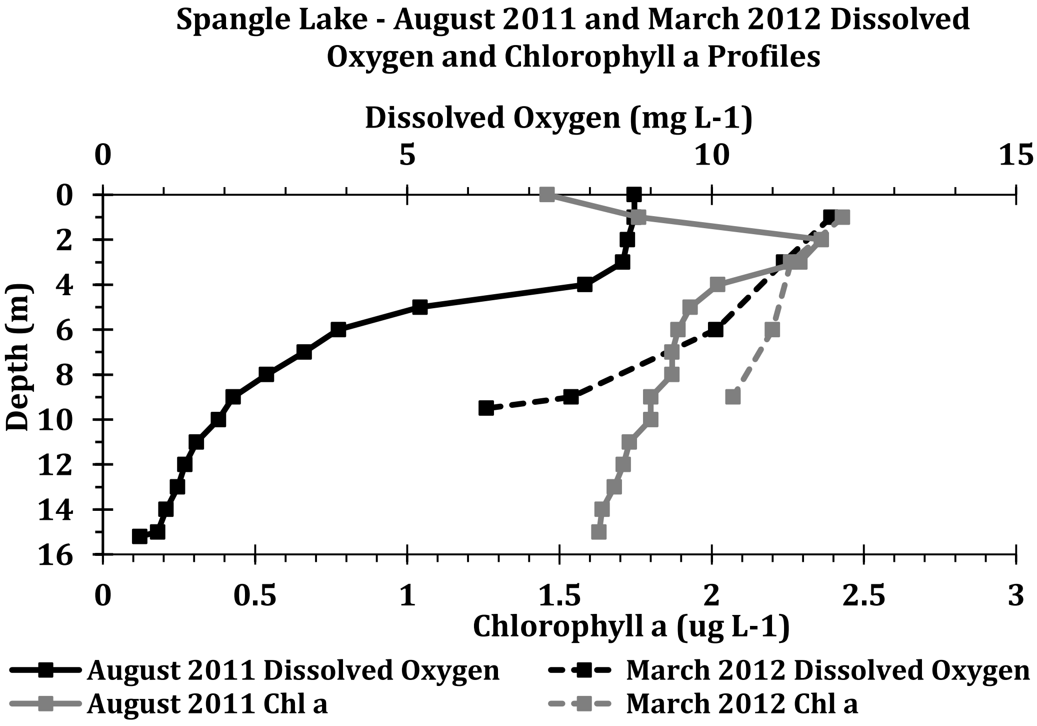


Figure 1.78. Spangle Lake DO and chl *a* profiles in Aug-2011 and Mar-2012.

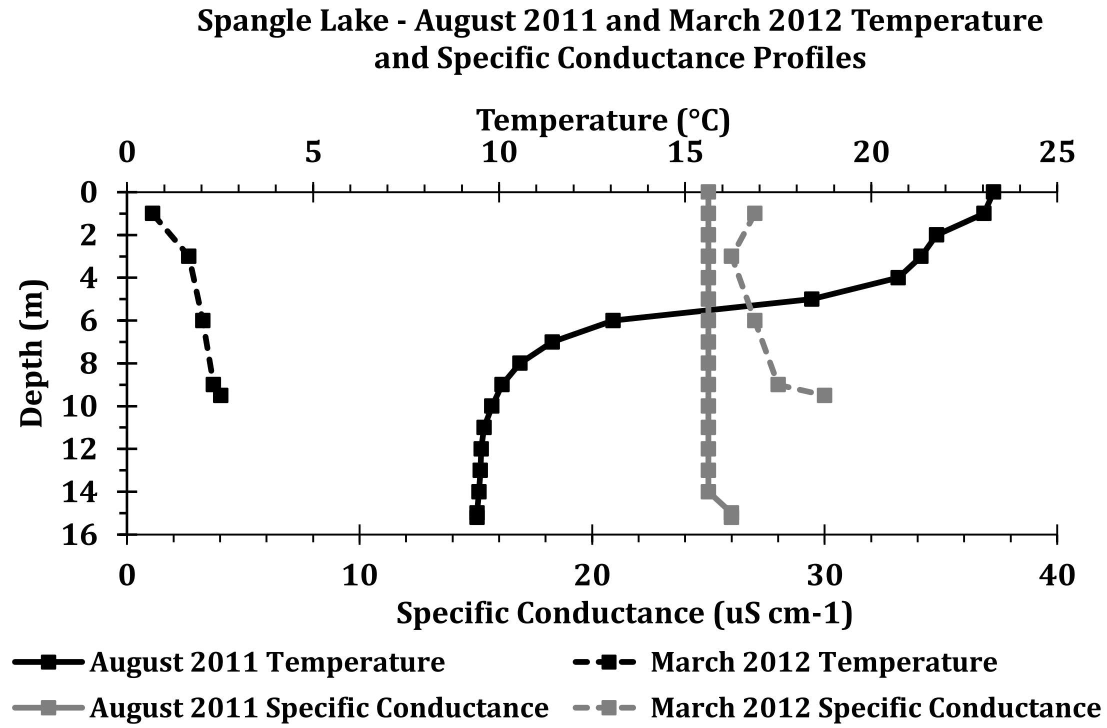


Figure 1.79. Spangle Lake temp and specific conductance profiles in Aug-2011 and Mar-2012.

Appendix B: Tables

Table 1.1: Water quality parameter concentrations for Lim Lake from 1983-2008.

Parameter	Baseline 1983[1]	AEA 1999[2]	EEM 2005[4]	EEM 2008[5]
Conductivity (μs cm^{-1})	33.5	2670[3]	1666	467
Sulphate (mg L^{-1})	No data	1300	841	509
Hardness (mg L^{-1})	25.5	1000	652	385
Calcium (mg L^{-1})	No data	400	355.5	132
Manganese (mg L^{-1})	No data	0.74	0.12	0.0301
Potassium (mg L^{-1})	No data	81	53.75	19.9
Sodium (mg L^{-1})	No data	190	145	59.4
Ammonia (mg L^{-1})	No data	13	5.03	0.44
Nitrate (mg L^{-1})	No data	11	6.45	1.67
Nitrite (mg L^{-1})	No data	0.3	0.18	No Data
Antimony (mg L^{-1})	<0.005	0.18	0.138	0.072
Arsenic (mg L^{-1})	<0.003	<0.005	<0.002	<0.001
Copper (mg L^{-1})	<0.001	0.009	0.0063	0.0055
Iron (mg L^{-1})	0.003	0.023	0.04	0.13
Lead (mg L^{-1})	<0.001	<0.0005	<0.005	0.001
Mercury (mg L^{-1})	<0.000015	0.00025	<0.0001	<0.0001
Molybdenum (mg L^{-1})	<0.020	0.25	0.07	0.044
Nickel (mg L$^{-1)}$	0.014	0.079	0.07	0.037
Zinc (mg L^{-1})	0.0175	0.034	0.019	0.008

[1] **Reference:** (Wood 1984), Table X and IX, Average of Sites LL1(1m and 4m) (close to outlet rather than deep zone).
[2] **Reference:** (Beak International Incorporated 2000*c*), Table 3.5, Site LIM-2 (closest to deep zone, 0.5m from bottom).
[3] **Reference:** (Beak International Incorporated 2000*c*), Table 3.3, Lim Lake (average of all in-lake samples in 1999).
[4] **Reference:** (Orr and Stecko 2006*a*), Table D.4, Lim Lake outlet (surface) (average from 2005, n=1 or 13, sample analyses was more comprehensive at outlet versus within lake).
[5] **Reference:** (Weech and Orr 2009*a*), Table D.3b, Lim Lake outlet (surface) (average from 2008, n=2, 12 or 13).

Table 1.2: Water quality parameter concentrations for Frank Lake from 1984-2008.

Parameter	Baseline 1984[1]	AEA 1992[2]	AEA 1999[3]	EEM 2005[5]	EEM 2008[6]
Conductivity (µs cm^{-1})	57.0	1970	2048[4]	2431	1503.8
Sulphate (mg L^{-1})	4.0	850.5	940	1135	722
Hardness (mg L^{-1})	26	847	810	743	520
Alkalinity (mg L^{-1})	7.9	19	30	21.1	22.2
Calcium (mg L^{-1})	7.85	331.5	320	294	154.14
Magnesium (mg L^{-1})	1.55	4.67	4.5	4.55	3.42
Manganese (mg L^{-1})	0.0205	0.5705	0.52	0.094	0.1282
Potassium (mg L^{-1})	0.4	63.05	68	73.07	50.62
Ammonia (mg L^{-1})	No data	6.775	4.01	4.065	1.038
Nitrate (mg L^{-1})	<0.005	11.4	12	21	17.648
Nitrite (mg L^{-1})	0.027	0.45	0.47	0.2	0.205
Antimony (mg L^{-1})	<0.001	0.337	0.22	0.13	0.056
Aluminum (mg L^{-1})	0.008	0.045	0.15	0.017	0.0702
Barium (mg L^{-1})	0.011	0.064	0.028	0.021	0.015
Copper (mg L^{-1})	0.003	<0.004	0.004	0.009	0.00462
Iron (mg L^{-1})	0.24	0.0175	0.17	0.095	0.1154
Molybdenum (mg L^{-1})	<0.005	0.42	0.4	0.371	0.120
Nickel (mg L^{-1})	0.0035	0.02	0.066	0.0525	0.037
Sodium (mg L^{-1})	0.95	78.5	120	198	127.3
Zinc (mg L^{-1})	0.0075	0.006	0.026	0.014	0.0061

[1] **Reference:** (SENES 1984), Table 3, Average of Sites F2(0.3m) and F2(20m) (closest to main channel deep zone).
[2] **Reference:** (ESP 1993), Table A-1, Average of Sites 3T(1m) and 3B(1m from bottom) (closest to main channel deep zone).
[3] **Reference:** (Beak International Incorporated 2000*a*), Table 3.4, Site FR2 (closest to main channel deep zone, 0.5m from bottom).
[4] **Reference:** (Beak International Incorporated 2000*a*), Table 3.2, Frank Lake (average of all in-lake samples in 1999).
[5] **Reference:** (Orr and Stecko 2006*b*), Table D.4, Frank Lake outlet (surface) (average from 2005, n=1, 5 or 6), sample analyses was more comprehensive at outlet versus within lake).
[6] **Reference:** (Weech and Orr 2009*b*), Table D.4, Frank Lake (surface) (average from 2008, n=4 or 5, not specified if outlet or within lake).

Table 1.3: Water quality parameter concentrations for Spangle Lake from 1984-2012.

Parameter	Baseline 1984[1]	AEA 1992[2]	AEA 1999[3]	EEM 2005[5]	EEM 2008[6]	Current Study 2011/12[7]	Current Study 2011 Inlet
Conductivity (µs cm^{-1})	50	32	25[4]	26.6	29.6	32.015	33.3
Sulphate (mg L^{-1})	4.5	5.59	4.2	3.0	2.3	1.961	1.64
Hardness (mg L^{-1})	14.8	13	16	11.46	13	14.464	14.81
Alkalinity (mg L^{-1})	5.15	12	6.8	5.6	8.6	10.180	10.7
Calcium (mg L^{-1})	4.2	3.71	4.6	3.54	5.22	4.235	4.30
Magnesium (mg L^{-1})	1.04	0.97	1.1	0.795	0.88	0.944	0.987
Manganese (mg L^{-1})	0.041	0.072	0.14	0.0114	0.022	0.042	0.0049
Potassium (mg L^{-1})	0.22	<0.4	<1.0	0.312	0.52	0.457	0.385
Ammonia (mg L^{-1})	0.034	0.04	0.06	<0.1	<0.05	0.028	0.077
Nitrate (mg L^{-1})	0.013	0.46	0.03	0.095	<0.03	0.073	<0.010
Nitrite (mg L^{-1})	<0.001	<0.03	<0.10	<0.01	<0.1	<0.009	<0.009
Antimony (mg L^{-1})	<0.005	<0.002	<0.002	<0.0001	<0.005	n/a	n/a
Aluminum (mg L^{-1})	<0.003	<0.025	0.36	0.18	0.14	0.140	0.116
Barium (mg L^{-1})	0.007	0.007	0.009	0.0068	<0.01	0.007	0.006
Copper (mg L^{-1})	<0.001	<0.003	<0.002	0.001	0.0018	0.004	<0.002
Iron (mg L^{-1})	0.16	0.319	0.65	0.166	0.16	0.231	0.082
Molybdenum (mg L^{-1})	<0.001	<0.01	<0.002	<0.01	<0.001	<0.040	<0.040
Nickel (mg L^{-1})	<0.001	<0.01	<0.002	<0.01	<0.002	<0.002	<0.002
Sodium (mg L^{-1})	0.55	2.48	0.66	0.56	0.502	0.739	0.7
Zinc (mg L^{-1})	0.007	0.002	0.0015	<0.01	0.0027	0.006	0.006

[1] **Reference:** (Harkness RA and Morgan JD 1985), Table 3, Average of Sites F2(0.3m) and F2(20m) (closest to main channel deep zone).

[2] **Reference:** (ESP 1993), Table A-1, Average of All Sites 3T (no map to distinguish sample which sample site was deep zone).

[3] **Reference:** (Beak International Incorporated 2000*a* and *c*), Table 3.5, Site SP3 (closest to main channel deep zone, 0.5m from bottom).

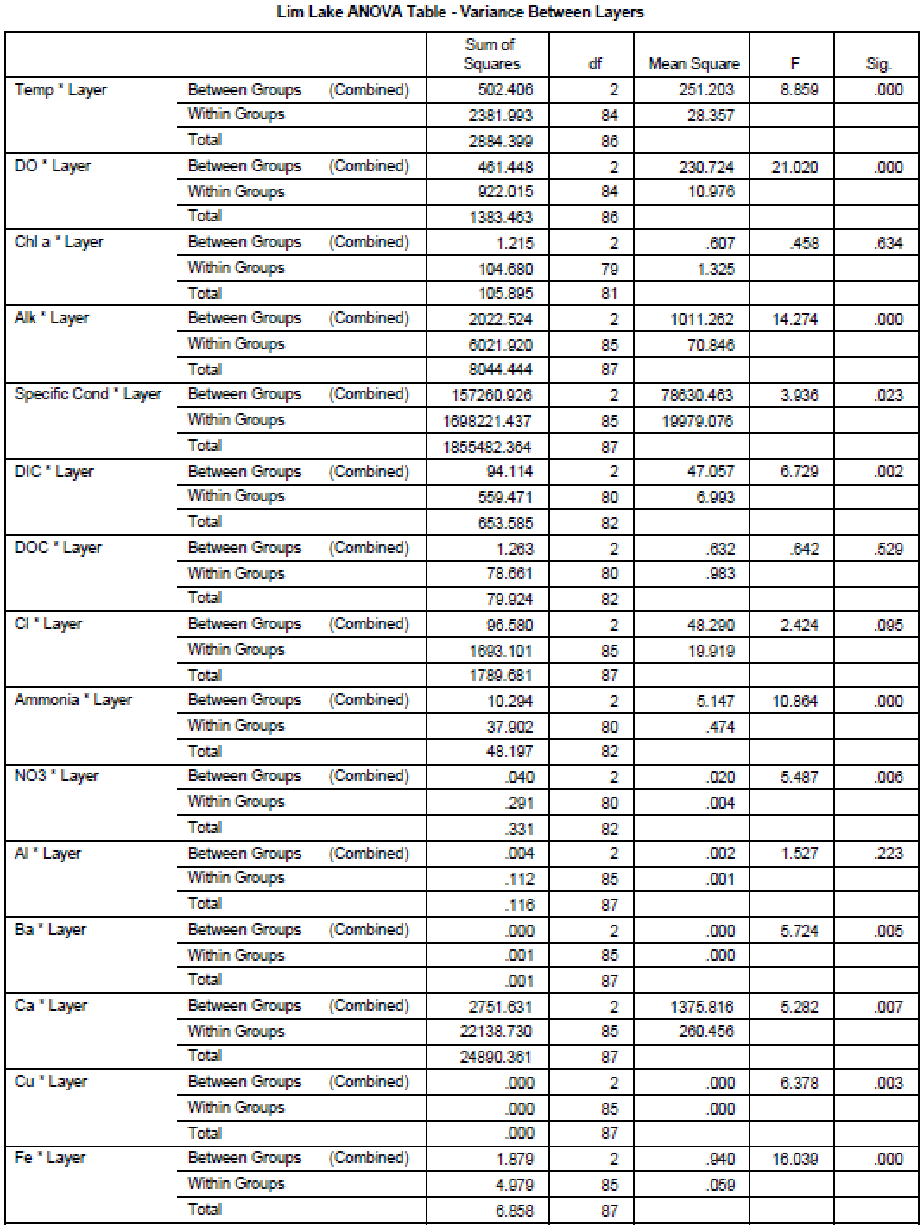
[4] **Reference:** (Beak International Incorporated 2000*a* and *c*), Table 3.3, Spangle Lake (average of all in-lake samples in 1999).

[5] **Reference:** (Orr and Stecko 2006*c*), Table D.1, Spangle Lake outlet (surface) (average from 2005, n=1 or 5), sample analyses was more comprehensive at outlet versus within lake).

[6] **Reference:** (Weech and Orr 2009*a*),Table D.3,Spangle Lake(surface) (average from 2008, n=1 or 5, not specified if outlet or within lake)

[7] **Collected during August 2011 and March 2012 of current study at 1, 2, 4, 7, 9 and 15m (averaged).**

Table 1.6. Lim Lake ANOVA results for variability significance between layers from Jul 2011-Nov 2013.



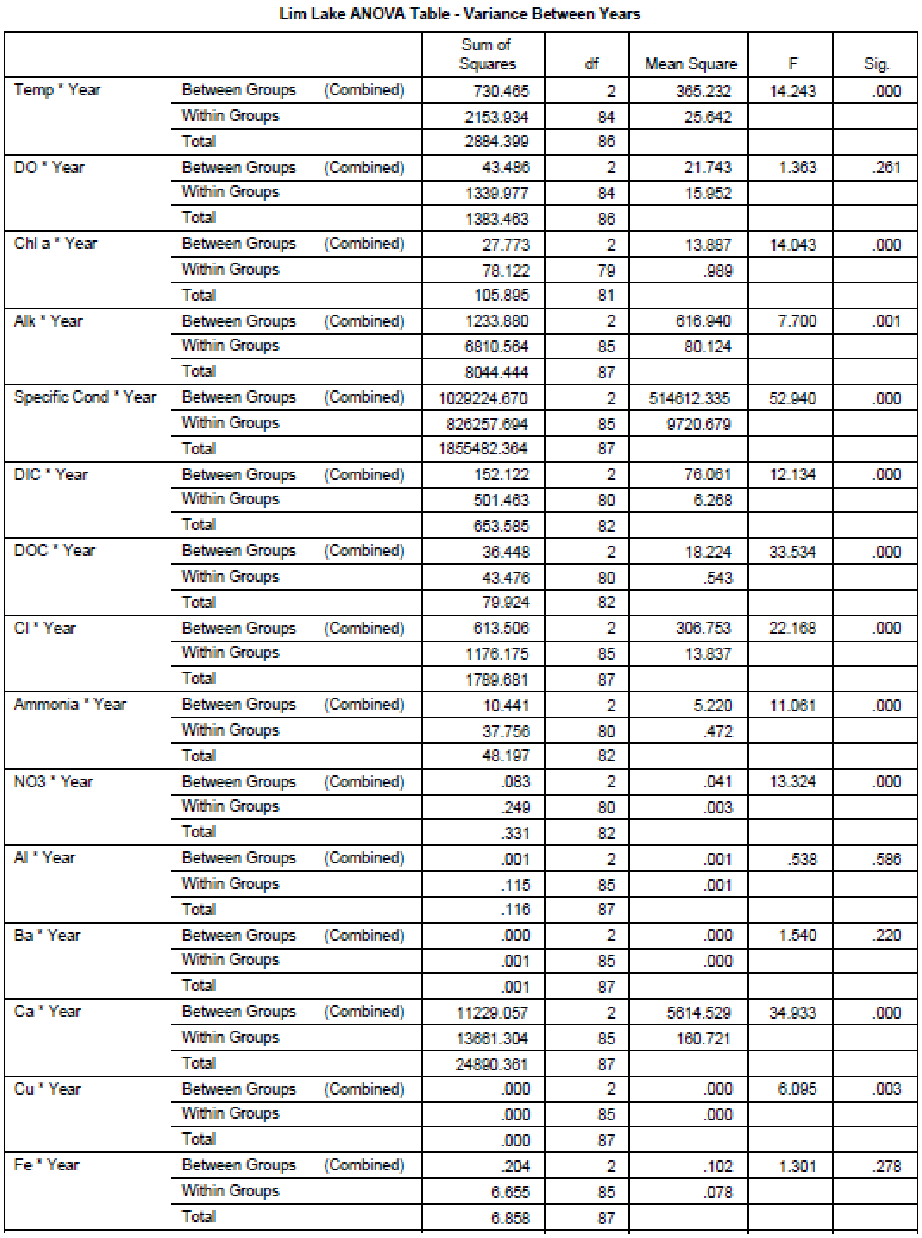
Lim Lake ANOVA Table - Variance Between Layers

			Sum of Squares	df	Mean Square	F	Sig.
Temp * Layer	Between Groups	(Combined)	502.406	2	251.203	8.859	.000
	Within Groups		2381.993	84	28.357		
	Total		2884.399	86			
DO * Layer	Between Groups	(Combined)	461.448	2	230.724	21.020	.000
	Within Groups		922.015	84	10.976		
	Total		1383.463	86			
Chl a * Layer	Between Groups	(Combined)	1.215	2	.607	.458	.634
	Within Groups		104.680	79	1.325		
	Total		105.895	81			
Alk * Layer	Between Groups	(Combined)	2022.524	2	1011.262	14.274	.000
	Within Groups		6021.920	85	70.846		
	Total		8044.444	87			
Specific Cond * Layer	Between Groups	(Combined)	157260.926	2	78630.463	3.936	.023
	Within Groups		1698221.437	85	19979.076		
	Total		1855482.364	87			
DIC * Layer	Between Groups	(Combined)	94.114	2	47.057	6.729	.002
	Within Groups		559.471	80	6.993		
	Total		653.585	82			
DOC * Layer	Between Groups	(Combined)	1.263	2	.632	.642	.529
	Within Groups		78.661	80	.983		
	Total		79.924	82			
Cl * Layer	Between Groups	(Combined)	96.580	2	48.290	2.424	.095
	Within Groups		1693.101	85	19.919		
	Total		1789.681	87			
Ammonia * Layer	Between Groups	(Combined)	10.294	2	5.147	10.864	.000
	Within Groups		37.902	80	.474		
	Total		48.197	82			
NO3 * Layer	Between Groups	(Combined)	.040	2	.020	5.487	.006
	Within Groups		.291	80	.004		
	Total		.331	82			
Al * Layer	Between Groups	(Combined)	.004	2	.002	1.527	.223
	Within Groups		.112	85	.001		
	Total		.116	87			
Ba * Layer	Between Groups	(Combined)	.000	2	.000	5.724	.005
	Within Groups		.001	85	.000		
	Total		.001	87			
Ca * Layer	Between Groups	(Combined)	2751.631	2	1375.816	5.282	.007
	Within Groups		22138.730	85	260.456		
	Total		24890.361	87			
Cu * Layer	Between Groups	(Combined)	.000	2	.000	6.378	.003
	Within Groups		.000	85	.000		
	Total		.000	87			
Fe * Layer	Between Groups	(Combined)	1.879	2	.940	16.039	.000
	Within Groups		4.979	85	.059		
	Total		6.858	87			

Lim Lake ANOVA Table - Variance Between Layers Continued

			Sum of Squares	df	Mean Square	F	Sig.
K * Layer	Between Groups	(Combined)	84.855	2	42.427	4.714	.011
	Within Groups		765.072	85	9.001		
	Total		849.927	87			
Mg * Layer	Between Groups	(Combined)	.989	2	.494	3.664	.030
	Within Groups		11.468	85	.135		
	Total		12.456	87			
Mn * Layer	Between Groups	(Combined)	1.286	2	.643	17.599	.000
	Within Groups		3.105	85	.037		
	Total		4.391	87			
Na * Layer	Between Groups	(Combined)	670.839	2	335.420	4.857	.010
	Within Groups		5869.719	85	69.056		
	Total		6540.558	87			
Ni * Layer	Between Groups	(Combined)	.000	2	.000	5.348	.006
	Within Groups		.000	85	.000		
	Total		.000	87			
Tot Sulphur * Layer	Between Groups	(Combined)	3297.674	2	1648.837	1.003	.371
	Within Groups		139790.429	85	1644.593		
	Total		143088.102	87			
Si * Layer	Between Groups	(Combined)	1.360	2	.680	5.944	.004
	Within Groups		7.779	68	.114		
	Total		9.139	70			
Sr * Layer	Between Groups	(Combined)	.003	2	.002	5.742	.005
	Within Groups		.024	85	.000		
	Total		.027	87			
Zn * Layer	Between Groups	(Combined)	.000	2	.000	1.339	.268
	Within Groups		.002	85	.000		
	Total		.002	87			
Sulphate * Layer	Between Groups	(Combined)	109271.564	2	54635.782	1.297	.279
	Within Groups		3579754.120	85	42114.754		
	Total		3689025.684	87			
pH * Layer	Between Groups	(Combined)	.889	2	.445	16.117	.000
	Within Groups		2.344	85	.028		
	Total		3.233	87			
TDS * Layer	Between Groups	(Combined)	72102.554	2	36051.277	3.849	.025
	Within Groups		796133.464	85	9366.276		
	Total		868236.018	87			
TKN * Layer	Between Groups	(Combined)	6.839	2	3.419	2.766	.069
	Within Groups		98.885	80	1.236		
	Total		105.723	82			
TotP * Layer	Between Groups	(Combined)	.001	2	.000	1.829	.167
	Within Groups		.017	80	.000		
	Total		.018	82			
Hardness * Layer	Between Groups	(Combined)	18242.444	2	9121.222	5.236	.007
	Within Groups		148059.555	85	1741.877		
	Total		166301.999	87			

Table 1.7. Lim Lake ANOVA results for variability significance between years from Jul 2011-Nov 2013.



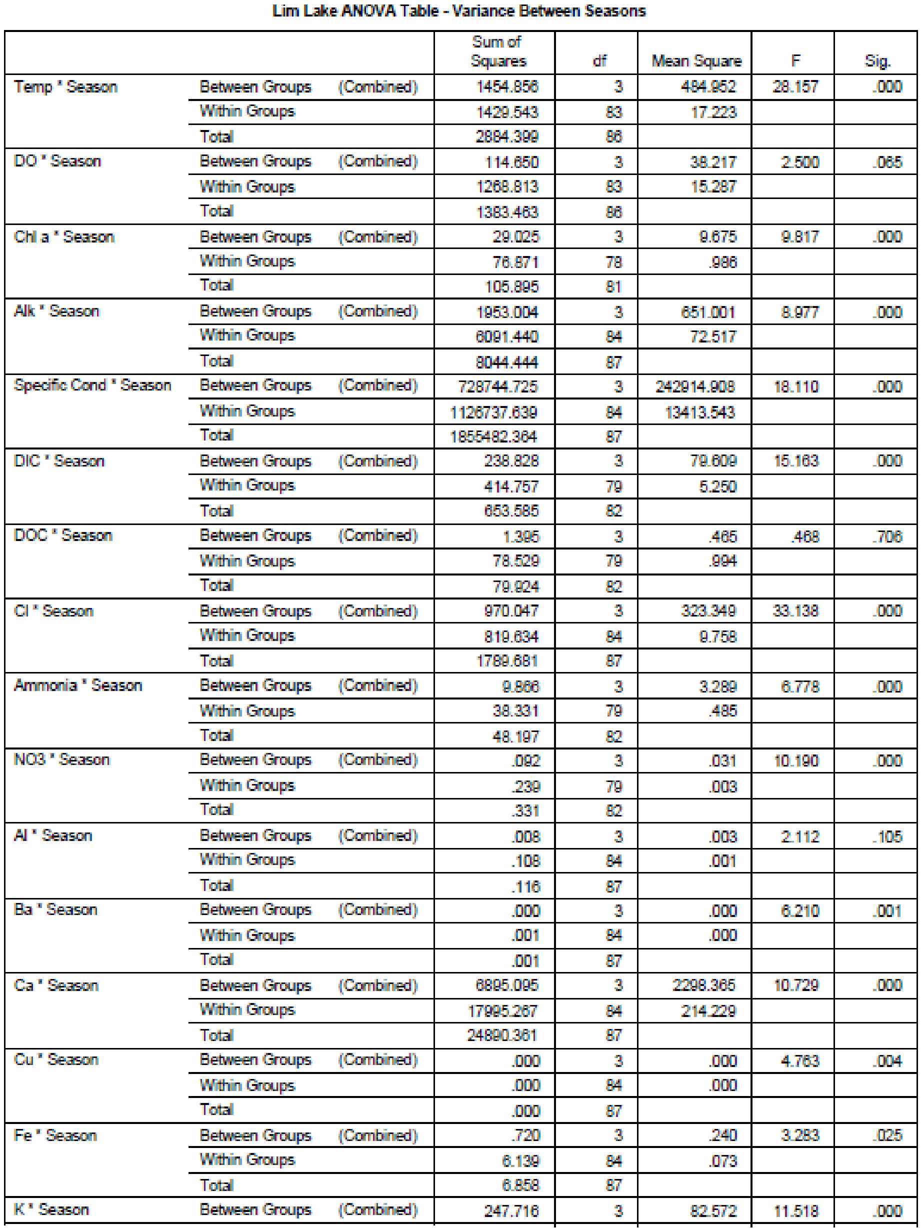
Lim Lake ANOVA Table - Variance Between Years

			Sum of Squares	df	Mean Square	F	Sig.
Temp * Year	Between Groups	(Combined)	730.465	2	365.232	14.243	.000
	Within Groups		2153.934	84	25.642		
	Total		2884.399	86			
DO * Year	Between Groups	(Combined)	43.486	2	21.743	1.363	.261
	Within Groups		1339.977	84	15.952		
	Total		1383.463	86			
Chl a * Year	Between Groups	(Combined)	27.773	2	13.887	14.043	.000
	Within Groups		78.122	79	.989		
	Total		105.895	81			
Alk * Year	Between Groups	(Combined)	1233.880	2	616.940	7.700	.001
	Within Groups		6810.564	85	80.124		
	Total		8044.444	87			
Specific Cond * Year	Between Groups	(Combined)	1029224.670	2	514612.335	52.940	.000
	Within Groups		826257.694	85	9720.679		
	Total		1855482.364	87			
DIC * Year	Between Groups	(Combined)	152.122	2	76.061	12.134	.000
	Within Groups		501.463	80	6.268		
	Total		653.585	82			
DOC * Year	Between Groups	(Combined)	36.448	2	18.224	33.534	.000
	Within Groups		43.476	80	.543		
	Total		79.924	82			
Cl * Year	Between Groups	(Combined)	613.506	2	306.753	22.168	.000
	Within Groups		1176.175	85	13.837		
	Total		1789.681	87			
Ammonia * Year	Between Groups	(Combined)	10.441	2	5.220	11.061	.000
	Within Groups		37.756	80	.472		
	Total		48.197	82			
NO3 * Year	Between Groups	(Combined)	.083	2	.041	13.324	.000
	Within Groups		.249	80	.003		
	Total		.331	82			
Al * Year	Between Groups	(Combined)	.001	2	.001	.538	.586
	Within Groups		.115	85	.001		
	Total		.116	87			
Ba * Year	Between Groups	(Combined)	.000	2	.000	1.540	.220
	Within Groups		.001	85	.000		
	Total		.001	87			
Ca * Year	Between Groups	(Combined)	11229.057	2	5614.529	34.933	.000
	Within Groups		13661.304	85	160.721		
	Total		24890.361	87			
Cu * Year	Between Groups	(Combined)	.000	2	.000	6.095	.003
	Within Groups		.000	85	.000		
	Total		.000	87			
Fe * Year	Between Groups	(Combined)	.204	2	.102	1.301	.278
	Within Groups		6.655	85	.078		
	Total		6.858	87			

Lim Lake ANOVA Table - Variance Between Years Continued

			Sum of Squares	df	Mean Square	F	Sig.
K * Year	Between Groups	(Combined)	411.825	2	205.913	39.951	.000
	Within Groups		438.101	85	5.154		
	Total		849.927	87			
Mg * Year	Between Groups	(Combined)	4.429	2	2.215	23.452	.000
	Within Groups		8.027	85	.094		
	Total		12.456	87			
Mn * Year	Between Groups	(Combined)	.291	2	.145	3.012	.054
	Within Groups		4.101	85	.048		
	Total		4.391	87			
Na * Year	Between Groups	(Combined)	3006.725	2	1503.363	36.161	.000
	Within Groups		3533.833	85	41.575		
	Total		6540.558	87			
Ni * Year	Between Groups	(Combined)	.000	2	.000	6.661	.002
	Within Groups		.000	85	.000		
	Total		.000	87			
Tot Sulphur * Year	Between Groups	(Combined)	54047.261	2	27023.631	25.797	.000
	Within Groups		89040.841	85	1047.539		
	Total		143088.102	87			
Si * Year	Between Groups	(Combined)	1.801	2	.901	8.347	.001
	Within Groups		7.337	68	.108		
	Total		9.139	70			
Sr * Year	Between Groups	(Combined)	.007	2	.003	14.079	.000
	Within Groups		.021	85	.000		
	Total		.027	87			
Zn * Year	Between Groups	(Combined)	.000	2	.000	1.628	.202
	Within Groups		.002	85	.000		
	Total		.002	87			
Sulphate * Year	Between Groups	(Combined)	968559.672	2	484279.836	15.131	.000
	Within Groups		2720466.012	85	32005.482		
	Total		3689025.684	87			
pH * Year	Between Groups	(Combined)	.359	2	.180	5.309	.007
	Within Groups		2.874	85	.034		
	Total		3.233	87			
TDS * Year	Between Groups	(Combined)	456350.066	2	228175.033	47.088	.000
	Within Groups		411885.952	85	4845.717		
	Total		868236.018	87			
TKN * Year	Between Groups	(Combined)	21.052	2	10.526	9.945	.000
	Within Groups		84.671	80	1.058		
	Total		105.723	82			
TotP * Year	Between Groups	(Combined)	.000	2	.000	.555	.576
	Within Groups		.018	80	.000		
	Total		.018	82			
Hardness * Year	Between Groups	(Combined)	74632.857	2	37316.429	34.602	.000
	Within Groups		91669.142	85	1078.460		
	Total		166301.999	87			

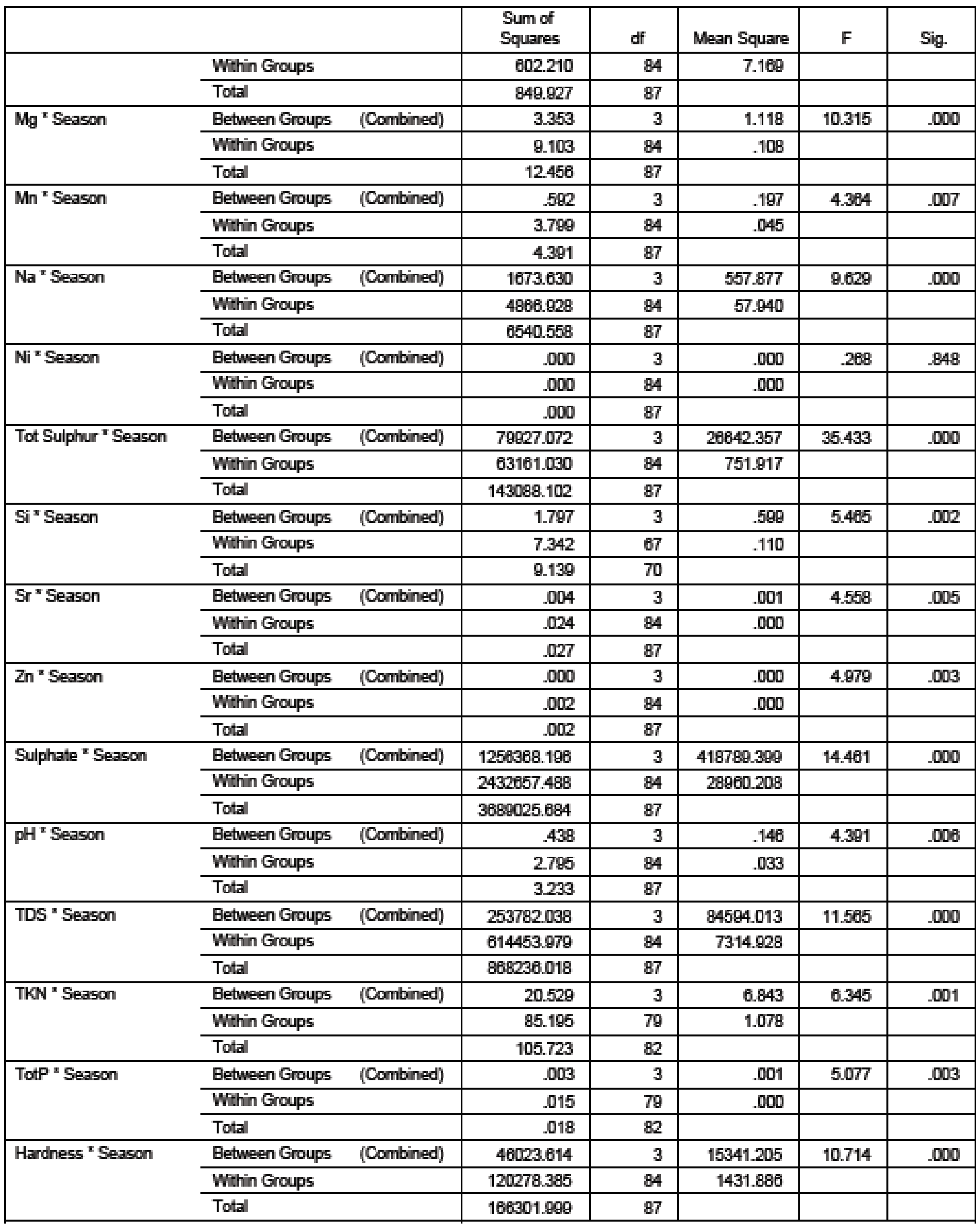
Table 1.8. Lim Lake ANOVA results for variability significance between seasons from Jul 2011-Nov 2013.



Lim Lake ANOVA Table - Variance Between Seasons

			Sum of Squares	df	Mean Square	F	Sig.
Temp * Season	Between Groups	(Combined)	1454.856	3	484.952	28.157	.000
	Within Groups		1429.543	83	17.223		
	Total		2884.399	86			
DO * Season	Between Groups	(Combined)	114.650	3	38.217	2.500	.065
	Within Groups		1268.813	83	15.287		
	Total		1383.463	86			
Chl a * Season	Between Groups	(Combined)	29.025	3	9.675	9.817	.000
	Within Groups		76.871	78	.986		
	Total		105.895	81			
Alk * Season	Between Groups	(Combined)	1953.004	3	651.001	8.977	.000
	Within Groups		6091.440	84	72.517		
	Total		8044.444	87			
Specific Cond * Season	Between Groups	(Combined)	728744.725	3	242914.908	18.110	.000
	Within Groups		1126737.639	84	13413.543		
	Total		1855482.364	87			
DIC * Season	Between Groups	(Combined)	238.828	3	79.609	15.163	.000
	Within Groups		414.757	79	5.250		
	Total		653.585	82			
DOC * Season	Between Groups	(Combined)	1.395	3	.465	.468	.706
	Within Groups		78.529	79	.994		
	Total		79.924	82			
Cl * Season	Between Groups	(Combined)	970.047	3	323.349	33.138	.000
	Within Groups		819.634	84	9.758		
	Total		1789.681	87			
Ammonia * Season	Between Groups	(Combined)	9.866	3	3.289	6.778	.000
	Within Groups		38.331	79	.485		
	Total		48.197	82			
NO3 * Season	Between Groups	(Combined)	.092	3	.031	10.190	.000
	Within Groups		.239	79	.003		
	Total		.331	82			
Al * Season	Between Groups	(Combined)	.008	3	.003	2.112	.105
	Within Groups		.108	84	.001		
	Total		.116	87			
Ba * Season	Between Groups	(Combined)	.000	3	.000	6.210	.001
	Within Groups		.001	84	.000		
	Total		.001	87			
Ca * Season	Between Groups	(Combined)	6895.095	3	2298.365	10.729	.000
	Within Groups		17995.267	84	214.229		
	Total		24890.361	87			
Cu * Season	Between Groups	(Combined)	.000	3	.000	4.763	.004
	Within Groups		.000	84	.000		
	Total		.000	87			
Fe * Season	Between Groups	(Combined)	.720	3	.240	3.283	.025
	Within Groups		6.139	84	.073		
	Total		6.858	87			
K * Season	Between Groups	(Combined)	247.716	3	82.572	11.518	.000

Lim Lake ANOVA Table - Variance Between Seasons Continued



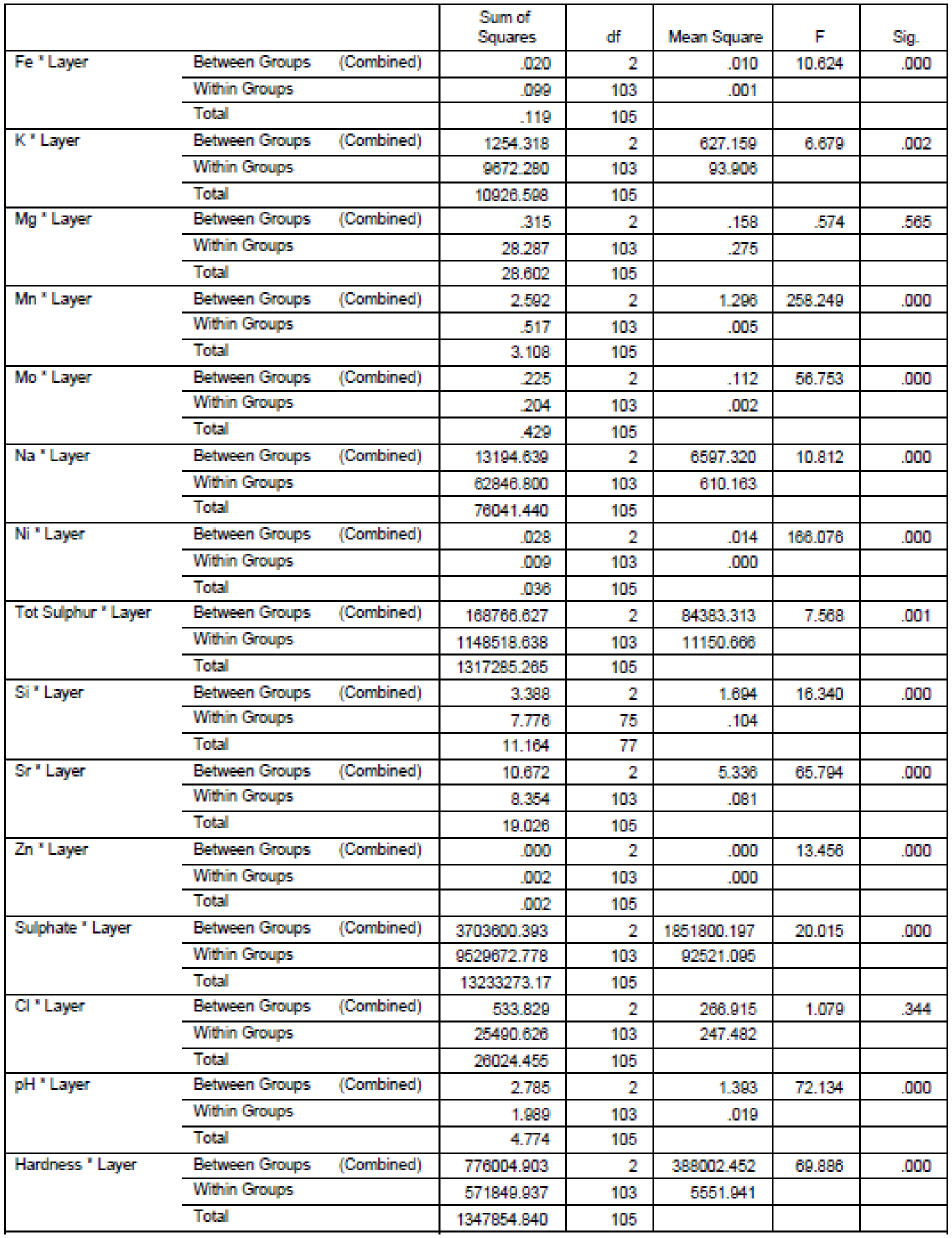
			Sum of Squares	df	Mean Square	F	Sig.
	Within Groups		602.210	84	7.169		
	Total		849.927	87			
Mg * Season	Between Groups	(Combined)	3.353	3	1.118	10.315	.000
	Within Groups		9.103	84	.108		
	Total		12.456	87			
Mn * Season	Between Groups	(Combined)	.592	3	.197	4.364	.007
	Within Groups		3.799	84	.045		
	Total		4.391	87			
Na * Season	Between Groups	(Combined)	1673.630	3	557.877	9.629	.000
	Within Groups		4866.928	84	57.940		
	Total		6540.558	87			
Ni * Season	Between Groups	(Combined)	.000	3	.000	.268	.848
	Within Groups		.000	84	.000		
	Total		.000	87			
Tot Sulphur * Season	Between Groups	(Combined)	79927.072	3	26642.357	35.433	.000
	Within Groups		63161.030	84	751.917		
	Total		143088.102	87			
Si * Season	Between Groups	(Combined)	1.797	3	.599	5.465	.002
	Within Groups		7.342	67	.110		
	Total		9.139	70			
Sr * Season	Between Groups	(Combined)	.004	3	.001	4.558	.005
	Within Groups		.024	84	.000		
	Total		.027	87			
Zn * Season	Between Groups	(Combined)	.000	3	.000	4.979	.003
	Within Groups		.002	84	.000		
	Total		.002	87			
Sulphate * Season	Between Groups	(Combined)	1256368.196	3	418789.399	14.461	.000
	Within Groups		2432657.488	84	28960.208		
	Total		3689025.684	87			
pH * Season	Between Groups	(Combined)	.438	3	.146	4.391	.006
	Within Groups		2.795	84	.033		
	Total		3.233	87			
TDS * Season	Between Groups	(Combined)	253782.038	3	84594.013	11.565	.000
	Within Groups		614453.979	84	7314.928		
	Total		868236.018	87			
TKN * Season	Between Groups	(Combined)	20.529	3	6.843	6.345	.001
	Within Groups		85.195	79	1.078		
	Total		105.723	82			
TotP * Season	Between Groups	(Combined)	.003	3	.001	5.077	.003
	Within Groups		.015	79	.000		
	Total		.018	82			
Hardness * Season	Between Groups	(Combined)	46023.614	3	15341.205	10.714	.000
	Within Groups		120278.385	84	1431.886		
	Total		166301.999	87			

Table 1.9. Frank Lake ANOVA results for variability significance between layers from Jul 2011-Nov 2013.

Frank Lake ANOVA Table - Variation Between Layers

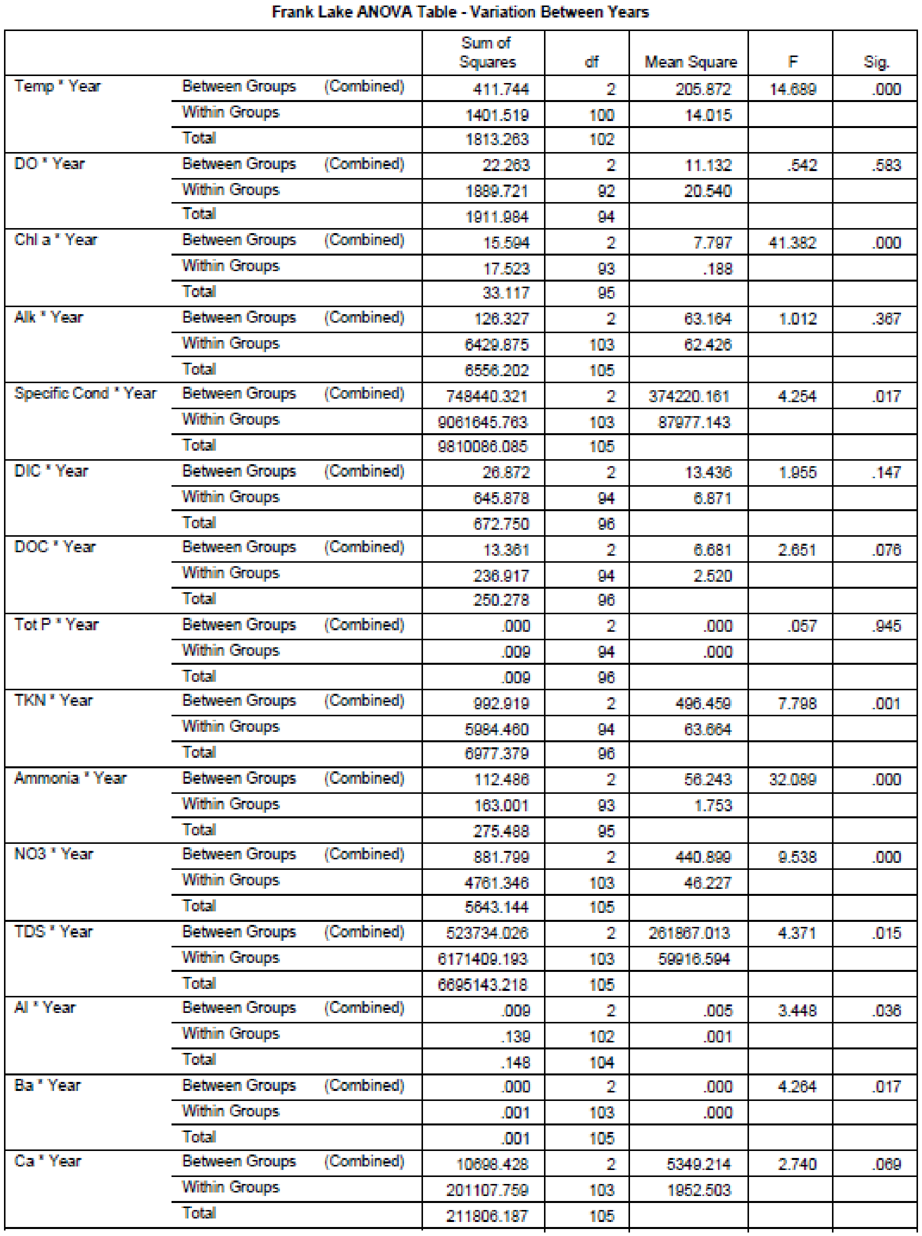
			Sum of Squares	df	Mean Square	F	Sig.
Temp * Layer	Between Groups	(Combined)	219.979	2	109.990	6.903	.002
	Within Groups		1593.284	100	15.933		
	Total		1813.263	102			
DO * Layer	Between Groups	(Combined)	1481.860	2	740.930	158.479	.000
	Within Groups		430.124	92	4.675		
	Total		1911.984	94			
Chl a * Layer	Between Groups	(Combined)	.856	2	.428	1.234	.296
	Within Groups		32.261	93	.347		
	Total		33.117	95			
Alk * Layer	Between Groups	(Combined)	4303.242	2	2151.621	98.367	.000
	Within Groups		2252.961	103	21.873		
	Total		6556.202	105			
Specific Cond * Layer	Between Groups	(Combined)	3601589.203	2	1800794.601	29.875	.000
	Within Groups		6208496.882	103	60276.669		
	Total		9810086.085	105			
DIC * Layer	Between Groups	(Combined)	145.204	2	72.602	12.936	.000
	Within Groups		527.547	94	5.612		
	Total		672.750	96			
DOC * Layer	Between Groups	(Combined)	14.293	2	7.147	2.847	.063
	Within Groups		235.985	94	2.510		
	Total		250.278	96			
Tot P * Layer	Between Groups	(Combined)	.001	2	.000	4.804	.010
	Within Groups		.008	94	.000		
	Total		.009	96			
TKN * Layer	Between Groups	(Combined)	465.221	2	232.610	3.358	.039
	Within Groups		6512.158	94	69.278		
	Total		6977.379	96			
Ammonia * Layer	Between Groups	(Combined)	25.245	2	12.622	4.691	.011
	Within Groups		250.243	93	2.691		
	Total		275.488	95			
NO3 * Layer	Between Groups	(Combined)	431.127	2	215.564	4.260	.017
	Within Groups		5212.017	103	50.602		
	Total		5643.144	105			
TDS * Layer	Between Groups	(Combined)	3374001.156	2	1687000.578	52.320	.000
	Within Groups		3321142.062	103	32244.098		
	Total		6695143.218	105			
Al * Layer	Between Groups	(Combined)	.013	2	.006	4.745	.011
	Within Groups		.136	102	.001		
	Total		.148	104			
Ba * Layer	Between Groups	(Combined)	.000	2	.000	33.007	.000
	Within Groups		.001	103	.000		
	Total		.001	105			
Ca * Layer	Between Groups	(Combined)	123942.983	2	61971.491	72.648	.000
	Within Groups		87863.204	103	853.041		
	Total		211806.187	105			

Frank Lake ANOVA Table - Variation Between Layers **Continued**



			Sum of Squares	df	Mean Square	F	Sig.
Fe * Layer	Between Groups	(Combined)	.020	2	.010	10.624	.000
	Within Groups		.099	103	.001		
	Total		.119	105			
K * Layer	Between Groups	(Combined)	1254.318	2	627.159	6.679	.002
	Within Groups		9672.280	103	93.906		
	Total		10926.598	105			
Mg * Layer	Between Groups	(Combined)	.315	2	.158	.574	.565
	Within Groups		28.287	103	.275		
	Total		28.602	105			
Mn * Layer	Between Groups	(Combined)	2.592	2	1.296	258.249	.000
	Within Groups		.517	103	.005		
	Total		3.108	105			
Mo * Layer	Between Groups	(Combined)	.225	2	.112	56.753	.000
	Within Groups		.204	103	.002		
	Total		.429	105			
Na * Layer	Between Groups	(Combined)	13194.639	2	6597.320	10.812	.000
	Within Groups		62846.800	103	610.163		
	Total		76041.440	105			
Ni * Layer	Between Groups	(Combined)	.028	2	.014	166.076	.000
	Within Groups		.009	103	.000		
	Total		.036	105			
Tot Sulphur * Layer	Between Groups	(Combined)	168766.627	2	84383.313	7.568	.001
	Within Groups		1148518.638	103	11150.666		
	Total		1317285.265	105			
Si * Layer	Between Groups	(Combined)	3.388	2	1.694	16.340	.000
	Within Groups		7.776	75	.104		
	Total		11.164	77			
Sr * Layer	Between Groups	(Combined)	10.672	2	5.336	65.794	.000
	Within Groups		8.354	103	.081		
	Total		19.026	105			
Zn * Layer	Between Groups	(Combined)	.000	2	.000	13.456	.000
	Within Groups		.002	103	.000		
	Total		.002	105			
Sulphate * Layer	Between Groups	(Combined)	3703600.393	2	1851800.197	20.015	.000
	Within Groups		9529672.778	103	92521.095		
	Total		13233273.17	105			
Cl * Layer	Between Groups	(Combined)	533.829	2	266.915	1.079	.344
	Within Groups		25490.626	103	247.482		
	Total		26024.455	105			
pH * Layer	Between Groups	(Combined)	2.785	2	1.393	72.134	.000
	Within Groups		1.989	103	.019		
	Total		4.774	105			
Hardness * Layer	Between Groups	(Combined)	776004.903	2	388002.452	69.886	.000
	Within Groups		571849.937	103	5551.941		
	Total		1347854.840	105			

Table 1.10. Frank Lake ANOVA results for variability significance between years from Jul 2011-Nov 2013.



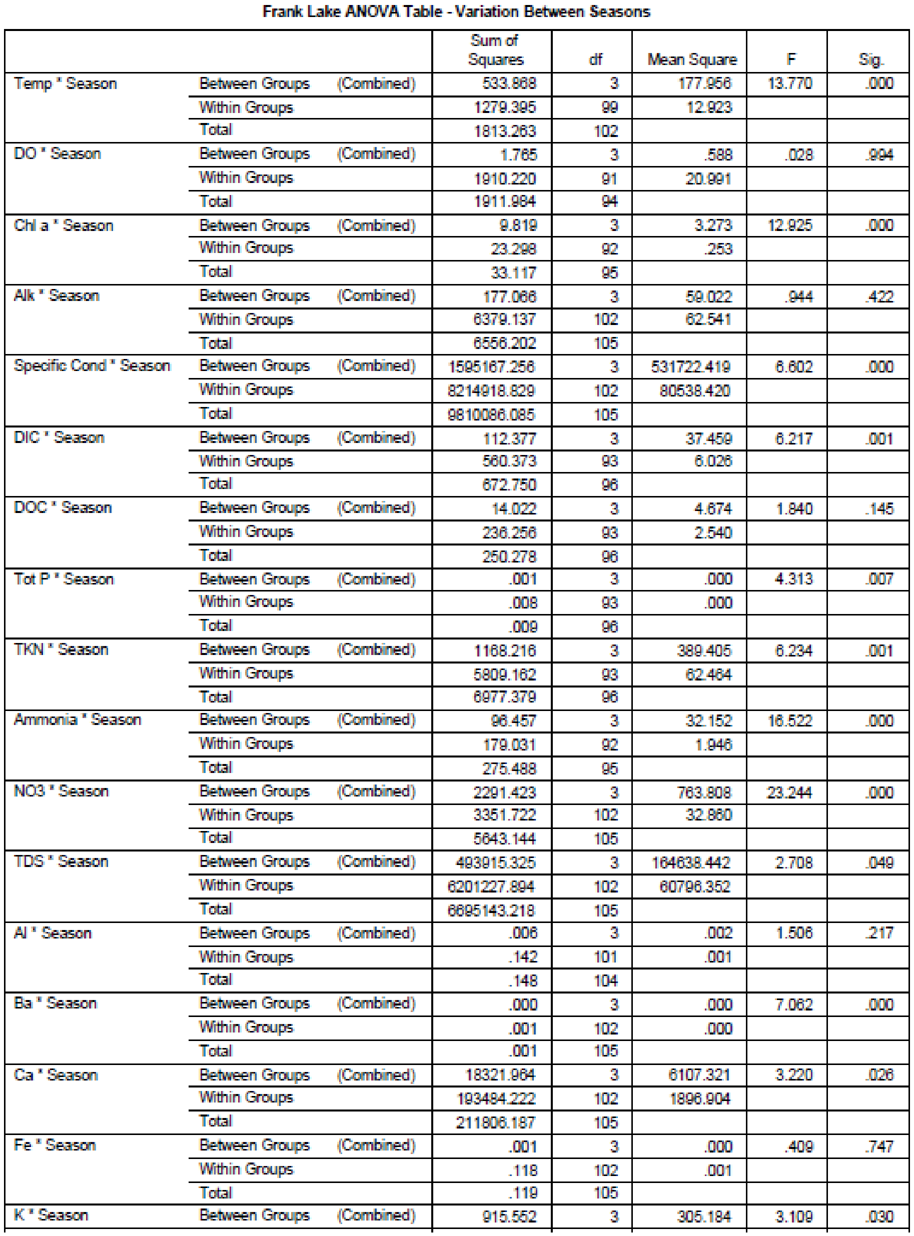
Frank Lake ANOVA Table - Variation Between Years

			Sum of Squares	df	Mean Square	F	Sig.
Temp * Year	Between Groups	(Combined)	411.744	2	205.872	14.689	.000
	Within Groups		1401.519	100	14.015		
	Total		1813.263	102			
DO * Year	Between Groups	(Combined)	22.263	2	11.132	.542	.583
	Within Groups		1889.721	92	20.540		
	Total		1911.984	94			
Chl a * Year	Between Groups	(Combined)	15.594	2	7.797	41.382	.000
	Within Groups		17.523	93	.188		
	Total		33.117	95			
Alk * Year	Between Groups	(Combined)	126.327	2	63.164	1.012	.367
	Within Groups		6429.875	103	62.426		
	Total		6556.202	105			
Specific Cond * Year	Between Groups	(Combined)	748440.321	2	374220.161	4.254	.017
	Within Groups		9061645.763	103	87977.143		
	Total		9810086.085	105			
DIC * Year	Between Groups	(Combined)	26.872	2	13.436	1.955	.147
	Within Groups		645.878	94	6.871		
	Total		672.750	96			
DOC * Year	Between Groups	(Combined)	13.361	2	6.681	2.651	.076
	Within Groups		236.917	94	2.520		
	Total		250.278	96			
Tot P * Year	Between Groups	(Combined)	.000	2	.000	.057	.945
	Within Groups		.009	94	.000		
	Total		.009	96			
TKN * Year	Between Groups	(Combined)	992.919	2	496.459	7.798	.001
	Within Groups		5984.460	94	63.664		
	Total		6977.379	96			
Ammonia * Year	Between Groups	(Combined)	112.486	2	56.243	32.089	.000
	Within Groups		163.001	93	1.753		
	Total		275.488	95			
NO3 * Year	Between Groups	(Combined)	881.799	2	440.899	9.538	.000
	Within Groups		4761.346	103	46.227		
	Total		5643.144	105			
TDS * Year	Between Groups	(Combined)	523734.026	2	261867.013	4.371	.015
	Within Groups		6171409.193	103	59916.594		
	Total		6695143.218	105			
Al * Year	Between Groups	(Combined)	.009	2	.005	3.448	.036
	Within Groups		.139	102	.001		
	Total		.148	104			
Ba * Year	Between Groups	(Combined)	.000	2	.000	4.264	.017
	Within Groups		.001	103	.000		
	Total		.001	105			
Ca * Year	Between Groups	(Combined)	10698.428	2	5349.214	2.740	.069
	Within Groups		201107.759	103	1952.503		
	Total		211806.187	105			

Frank Lake ANOVA Table - Variation Between Years **Continued**

			Sum of Squares	df	Mean Square	F	Sig.
Fe * Year	Between Groups	(Combined)	.006	2	.003	2.529	.085
	Within Groups		.114	103	.001		
	Total		.119	105			
K * Year	Between Groups	(Combined)	980.522	2	490.261	5.077	.008
	Within Groups		9946.076	103	96.564		
	Total		10926.598	105			
Mg * Year	Between Groups	(Combined)	5.151	2	2.575	11.312	.000
	Within Groups		23.451	103	.228		
	Total		28.602	105			
Mn * Year	Between Groups	(Combined)	.014	2	.007	.227	.798
	Within Groups		3.095	103	.030		
	Total		3.108	105			
Mo * Year	Between Groups	(Combined)	.048	2	.024	6.497	.002
	Within Groups		.381	103	.004		
	Total		.429	105			
Na * Year	Between Groups	(Combined)	2839.501	2	1419.750	1.998	.141
	Within Groups		73201.939	103	710.698		
	Total		76041.440	105			
Ni * Year	Between Groups	(Combined)	.001	2	.000	1.273	.284
	Within Groups		.035	103	.000		
	Total		.036	105			
Tot Sulphur * Year	Between Groups	(Combined)	237617.619	2	118808.809	11.334	.000
	Within Groups		1079667.646	103	10482.210		
	Total		1317285.265	105			
Si * Year	Between Groups	(Combined)	1.115	2	.557	4.159	.019
	Within Groups		10.049	75	.134		
	Total		11.164	77			
Sr * Year	Between Groups	(Combined)	.035	2	.018	.096	.908
	Within Groups		18.990	103	.184		
	Total		19.026	105			
Zn * Year	Between Groups	(Combined)	.000	2	.000	.651	.524
	Within Groups		.002	103	.000		
	Total		.002	105			
Sulphate * Year	Between Groups	(Combined)	725793.048	2	362896.524	2.988	.055
	Within Groups		12507480.12	103	121431.846		
	Total		13233273.17	105			
Cl * Year	Between Groups	(Combined)	2271.411	2	1135.705	4.925	.009
	Within Groups		23753.044	103	230.612		
	Total		26024.455	105			
pH * Year	Between Groups	(Combined)	.100	2	.050	1.101	.336
	Within Groups		4.674	103	.045		
	Total		4.774	105			
Hardness * Year	Between Groups	(Combined)	70998.256	2	35499.128	2.864	.062
	Within Groups		1276856.584	103	12396.666		
	Total		1347854.840	105			

Table 1.11. Frank Lake ANOVA results for variability significance between seasons from Jul 2011-Nov 2013.



Frank Lake ANOVA Table - Variation Between Seasons

			Sum of Squares	df	Mean Square	F	Sig.
Temp * Season	Between Groups	(Combined)	533.868	3	177.956	13.770	.000
	Within Groups		1279.395	99	12.923		
	Total		1813.263	102			
DO * Season	Between Groups	(Combined)	1.765	3	.588	.028	.994
	Within Groups		1910.220	91	20.991		
	Total		1911.984	94			
Chl a * Season	Between Groups	(Combined)	9.819	3	3.273	12.925	.000
	Within Groups		23.298	92	.253		
	Total		33.117	95			
Alk * Season	Between Groups	(Combined)	177.066	3	59.022	.944	.422
	Within Groups		6379.137	102	62.541		
	Total		6556.202	105			
Specific Cond * Season	Between Groups	(Combined)	1595167.256	3	531722.419	6.602	.000
	Within Groups		8214918.829	102	80538.420		
	Total		9810086.085	105			
DIC * Season	Between Groups	(Combined)	112.377	3	37.459	6.217	.001
	Within Groups		560.373	93	6.026		
	Total		672.750	96			
DOC * Season	Between Groups	(Combined)	14.022	3	4.674	1.840	.145
	Within Groups		236.256	93	2.540		
	Total		250.278	96			
Tot P * Season	Between Groups	(Combined)	.001	3	.000	4.313	.007
	Within Groups		.008	93	.000		
	Total		.009	96			
TKN * Season	Between Groups	(Combined)	1168.216	3	389.405	6.234	.001
	Within Groups		5809.162	93	62.464		
	Total		6977.379	96			
Ammonia * Season	Between Groups	(Combined)	96.457	3	32.152	16.522	.000
	Within Groups		179.031	92	1.946		
	Total		275.488	95			
NO3 * Season	Between Groups	(Combined)	2291.423	3	763.808	23.244	.000
	Within Groups		3351.722	102	32.860		
	Total		5643.144	105			
TDS * Season	Between Groups	(Combined)	493915.325	3	164638.442	2.708	.049
	Within Groups		6201227.894	102	60796.352		
	Total		6695143.218	105			
Al * Season	Between Groups	(Combined)	.006	3	.002	1.506	.217
	Within Groups		.142	101	.001		
	Total		.148	104			
Ba * Season	Between Groups	(Combined)	.000	3	.000	7.062	.000
	Within Groups		.001	102	.000		
	Total		.001	105			
Ca * Season	Between Groups	(Combined)	18321.964	3	6107.321	3.220	.026
	Within Groups		193484.222	102	1896.904		
	Total		211806.187	105			
Fe * Season	Between Groups	(Combined)	.001	3	.000	.409	.747
	Within Groups		.118	102	.001		
	Total		.119	105			
K * Season	Between Groups	(Combined)	915.552	3	305.184	3.109	.030

Frank Lake ANOVA Table - Variation Between Seasons Continued

			Sum of Squares	df	Mean Square	F	Sig.
	Within Groups		10011.046	102	98.148		
	Total		10926.598	105			
Mg * Season	Between Groups	(Combined)	5.948	3	1.983	8.928	.000
	Within Groups		22.654	102	.222		
	Total		28.602	105			
Mn * Season	Between Groups	(Combined)	.049	3	.016	.549	.650
	Within Groups		3.059	102	.030		
	Total		3.108	105			
Mo * Season	Between Groups	(Combined)	.034	3	.011	2.947	.036
	Within Groups		.395	102	.004		
	Total		.429	105			
Na * Season	Between Groups	(Combined)	4050.375	3	1350.125	1.913	.132
	Within Groups		71991.065	102	705.795		
	Total		76041.440	105			
Ni * Season	Between Groups	(Combined)	.001	3	.000	1.064	.368
	Within Groups		.035	102	.000		
	Total		.036	105			
Tot Sulphur * Season	Between Groups	(Combined)	533544.381	3	177848.127	23.146	.000
	Within Groups		783740.884	102	7683.734		
	Total		1317285.265	105			
Si * Season	Between Groups	(Combined)	2.312	3	.771	6.444	.001
	Within Groups		8.851	74	.120		
	Total		11.164	77			
Sr * Season	Between Groups	(Combined)	.157	3	.052	.283	.837
	Within Groups		18.869	102	.185		
	Total		19.026	105			
Zn * Season	Between Groups	(Combined)	.000	3	.000	7.692	.000
	Within Groups		.002	102	.000		
	Total		.002	105			
Sulphate * Season	Between Groups	(Combined)	4591795.367	3	1530598.456	18.066	.000
	Within Groups		8641477.805	102	84720.371		
	Total		13233273.17	105			
Cl * Season	Between Groups	(Combined)	10733.709	3	3577.903	23.867	.000
	Within Groups		15290.746	102	149.909		
	Total		26024.455	105			
pH * Season	Between Groups	(Combined)	.066	3	.022	.476	.700
	Within Groups		4.708	102	.046		
	Total		4.774	105			
Hardness * Season	Between Groups	(Combined)	120982.778	3	40327.593	3.353	.022
	Within Groups		1226872.062	102	12028.157		
	Total		1347854.840	105			

Table 1.12. Average, maximum and minimum parameter concentrations at Lim Lake inlet during 2012 (n=2) and 2013 (n=7). All units are mg L^{-1} except pH and Sp-cond ($\mu S\ cm^{-1}$). All data from water samples.

		2012			2013		
Parameter	**PWQO**	**Avg ± StDev**	**Max**	**Min**	**Avg ± StDev**	**Max**	**Min**
Alk	n/a	9.05 ± 1.48	10.10	8.00	8.24 ± 1.26	9.70	6.30
pH	6.5-8.5	6.18 ± 0.13	6.27	6.09	6.04 ± 0.08	6.17	5.97
Sp-Cond	n/a	34.20 ± 3.39	36.60	31.80	33.64 ± 5.76	39.30	25.80
TDS	n/a	96.2 ± 29.9	117.4	75	76.1 ± 12.8	94.4	60.4
Hardness	n/a	20.03 ± 1.88	21.36	18.71	18.05 ± 1.77	21.49	18.05
DOC	n/a	16.4 ± 11.9	24.8	8	25.42 ± 6.6	32.6	19.2
DIC	n/a	4.82 ± 6.05	9.1	0.54	2.45 ± 0.09	2.51	2.38
SO_4	n/a	2.86 ± 0.23	3.02	2.69	1.41 ± 0.34	1.74	0.93
Total Sulphur	n/a	1.22 ± 0.007	1.22	1.21	0.696 ± 0.08	0.79	0.56
Ca	n/a	6.14 ± 0.61	6.58	5.71	5.40 ± 0.64	6.59	4.64
Na	n/a	1.00 ± 1.06	0.93	1.08	1.07 ± 0.24	1.32	0.74
K	n/a	0.28 ± 0.01	0.29	0.27	0.23 ± 0.17	0.43	0.05
Mg	n/a	1.14 ± 0.85	1.20	1.08	1.11 ± 0.06	1.31	0.89
Cl	n/a	0.43 ± 0.00	0.43	0.43	0.32 ± 0.12	0.49	0.20
Al	0.075	0.474 ± 0.09	0.541	0.407	0.468 ± 0.09	0.612	0.378
Fe	0.30	0.349 ± 0.11	0.429	0.268	0.39 ± 0.07	0.49	0.27
Mn	n/a	0.0013±0.0011	0.002	0.0005	0.0023±0.008	0.0036	0.0008
Si	n/a	1.323 ± 0.43	1.628	1.018	1.265 ± 0.007	1.27	1.26
Zn	0.02	0.0085±0.0007	0.009	0.008	0.0077±0.003	0.014	0.005
NO_3	n/a	0.11 ± 0.03	0.13	0.09	0.14 ± 0.06	0.2	0.06
NH_3	n/a	<DL	<DL	<DL	0.050 ± 0.0	0.053	0.048

Table 1.13. Average, maximum and minimum parameter concentrations at Frank Lake inlet during 2011 (n=5), 2012 (n=2) and 2013 (n=7). All units are mg L^{-1} except pH and Sp-cond (µS cm^{-1}). All data from water samples.

		2011			**2012**			**2013**		
Parameter	**PWQO**	**Avg ± StDev**	**Max**	**Min**	**Avg ± StDev**	**Max**	**Min**	**Avg ± StDev**	**Max**	**Min**
Alk	n/a	38.1±3.8	43.3	34	16.6±3.3	18.9	14.3	28.0±11.9	40.2	10.7
pH	6.5-8.5	7.1±0.08	7.3	7.0	6.7±0.07	6.8	6.7	6.9±0.4	7.3	6.4
Sp-Cond	n/a	2406±446	2710	1710	168.5±85	229	108.1	935.9±1058	2090	60.1
TDS	n/a	1722±259	1919	1316	132.8±36.2	158.4	107.2	653.2±705	1414	71.1
Hardness	n/a	518±82.4	598.5	409.4	40±14.7	50.4	29.6	212.7±227	474.5	22.4
SO_4	n/a	1222±592	1788	538	50.2±35	75.2	25.3	324.3±395	778	3.0
Total Sulphur	n/a	479±252	759.2	243.8	14±7.8	19.6	8.4	112.58±134	263.2	3.5
DOC	n/a	2.6±0.07	2.7	2.5	11.6±11	19.4	3.8	15.3±5.1	21.9	9.3
DIC	n/a	7.95±2.4	9.5	3.9	5.5±5.0	9.0	1.8	4.6±2.5	8.9	1.0
Ca	n/a	199.7±32.2	231.3	157.5	14.4±5.7	18.4	10.3	82±88.7	184.3	8.02
Na	n/a	204.8±37	234.8	151	13.5±7.5	18.7	8.2	77.5±89.9	187.4	4.5
K	n/a	98.7±19.9	114.4	69.6	6.3±2.9	8.4	4.2	33.2±36.8	75.6	2.7
Cl	n/a	91.6±46.4	138.7	40	3.5±2.9	5.6	1.5	24±29.2	55.8	0.3
Mg	n/a	4.7±0.6	5.3	3.9	1±0.1	1.08	0.9	1.9±1.4	3.5	0.6
Si	n/a	0.904±0.355	1.497	0.579	2.345±1.142	3.154	1.538	0.530±0.753	1.40	0.090
Mo	0.04	0.202±0.055	0.243	0.106	0.078±0.001	0.078	0.077	0.123±0.055	0.19	0.061
Al	0.075	0.11±0.1	0.22	0.014	0.24±0.052	0.28	0.207	0.017±0.004	0.022	0.012
Cu	0.005	0.006±0.002	0.007	0.003	0.015±0.01	0.016	0.014	0.014±0.004	0.018	0.009
Mn	n/a	0.027±0.01	0.037	0..015	0.029±0.031	0.051	0.007	0.051±0.024	0.089	0.021
Ni	0.025	0.035±0.014	0.050	0.020	0.020±0.007	0.025	0.015	0.033±0.014	0.059	0.017
Fe	0.30	0.05±0.024	0.077	0.026	0.192±109	0.27	0.12	0.141±0.124	0.284	0.012
Zn	0.02	0.006±0.006	0.017	0.002	0.0055±0.0007	0.006	0.005	0.0037±0.002	0.007	0.0010
NO_3	n/a	37.15±17.6	54.43	18.0	0.767±0.218	0.921	0.613	12.478±11.35	22.55	0.229
NH_4	n/a	8.85±4.12	12.53	2.898	<DL	<DL	<DL	1.769±1.953	3.665	0.076

Table 1.14. Average parameter concentrations in Lim Lake during fall 2011 (n=6), 2012 (n=) and 2013 (n=5) turnover and percent change from fall 2011 to fall 2013 (negative % indicates an decrease). ± represents standard deviation. All units are mg L^{-1} except pH and Sp-cond (μS cm^{-1}). *multi-probe data. †data from June 2013 and percent decrease from fall 2011-June 2013.

Parameter	Fall 2011	Fall 2012	Fall 2013	% Change 2011 to 2013
Alk	39.53 ± 0.27	33.85 ± 0.61	31.78 ± 0.08	-19.60
pH*	7.034 ± 0.01	7.33 ± 0.10	7.033 ± 0.06	-0.015
Sp-Cond*	653.83 ± 0.39	507.46 ± 4.33	343.08 ± 3.01	-47.53
TDS	449.3 ± 5.14	357.3 ± 42.9	238.6 ± 1.3	-46.90
Hardness	218.58 ± 2.99	182.2 ± 2.88	122.60 ± 1.40	-43.91
DOC	8.26 ± 0.19	8.13 ± 0.23	9.88 ± 0.36†	19.65†
DIC	9.26 ± 0.51	9.08 ± 0.41	5.62± 11.54†	-39.33†
SO_4	351.33 ± 1.06	286.07 ± 5.77	107.73 ± 1.09	-69.34
Total Sulphur	87.07 ± 1.32	61.89 ± 8.19	40.66 ± 0.91	-53.30
Ca	82.61 ± 1.29	64.89 ± 9.13	45.51 ± 0.50	-44.91
Na	38.14 ± 0.57	28.29 ± 3.84	17.49 ± 0.40	-54.14
K	13.30 ± 0.20	9.72 ± 1.30	6.64 ± 0.15	-50.03
Mg	2.99 ± 0.04	2.57 ± 0.32	2.18 ± 0.04	-27.11
Cl	16.67 ± 0.04	11.82 ± 0.88	8.13 ± 0.56	-51.22
Al	0.0387 ± 0.01	0.0452 ± 0.01	0.0448 ± 0.00	15.72
Cu	0.003 ± 0.0	0.0033 ± 0.0	0.0034 ± 0.0	13.33
Fe	0.102 ± 0.001	0.071 ± 0.02	0.170 ± 0.004	66.86
Mn	0.14 ± 0.0	0.09 ± 0.01	0.09 ± 0.0	-37.42
Si	0.168 ± 0.005	0.397 ± 0.253	0.85 ± 0.136†	408.11†
Zn	0.0036 ± 0.001	0.005 ± 0.001	0.0054 ± 0.002	51.20
NO_3	0.013 ± 0.004	0.14 ± 0.009	0.01 ± 0.0	-92.25
NH_3	0.41 ± 0.03	0.36 ± 0.06	0.23 ± 0.08†	-42.52†

Table 1.15. Average parameter concentrations on Frank Lake mixo- and monimolimnion during fall 2011 (mix: n=3, moni: n=4), 2012 (mix: n=3, moni: n=5) and 2013 (mix: n=2, moni: n=7) turnover and percent change from fall 2011 to fall 2013 (negative % indicates a decrease). Mixolimnion depths included. ± represents standard deviation. All units are mg L^{-1} except pH and Sp-cond (µS cm^{-1}). *multi-probe data, variable n. † data from June 2013and percent decrease from fall 2011-June 2013.

	Fall 2011 Average		**Fall 2012 Average**		**Fall 2013 Average**		**% Change 2011-2013**	
Parameter	**Mix =11m**	**Moni**	**Mix=9m**	**Moni**	**Mix=6m**	**Moni**	**Mix**	**Moni**
Alk	36.8±2.0	44.0±0.5	27.9±0.9	38.7±7.1	29.6±0.1	38.7±9.2	-19.6	-12.0
pH*	6.9±0.03, n=12	6.1±0.1, n=16	7.4±0.1, n=10	6.5±0.1, n=16	7.1±0.04, n=6	6.5±0.1, n=20	3.1	6.4
Sp-Cond*	2071±2	2228±24	1842±22	2146±51	1513±45	2032±138	-26.9	-8.8
TDS	1534±4.5	1750±12.3	1344±24.3	1606±99	1086±5.8	1424±208	-29.2	-18.6
Hardness	478.7±24	626.1±21.9	416.9±4.1	505.7±42.7	343.1±2.7	463.6±92.5	-28.3	-26.0
SO_4	1268.5±2.8	1562.9±23.6	1032.8±68.6	1392.8±135.4	554.2±1.9	816.6±165.2	-56.3	-47.8
Tot Sul	288.1±3.8	362.6±17.5	253.4±3.0	303.3±19.8	196.6±1.1	265.7±45.5	-31.8	-26.7
DOC	4.1±0.1	5±0.1	4±0.1	4.4±0.4	10.2±4.3†	5.3±0.6†	145.0†	5.5†
DIC	8.6±0.4	12.7±1.2	8.2±0.2	9.8±1.2	2.8±2.3†	8.1±3.3†	-67.9†	-35.7†
Ca	184.0±9.6	243.5±8.3	160.3±1.6	195.6±17.0	132.3±1.03	179.6±36.6	-28.1	-26.2
Na	179.1±2.2	176.3±4.7	181.6±2.1	192.2±6.0	117.9±0.4	138.5±8.7	-34.2	-21.4
K	81.6±1.1	77.3±2.8	74.2±0.9	77.7±3.1	55.2±0.3	66.7±4.7	-32.4	-13.7
Cl	77.8±0.2	60.0±0.9	58.4±3.4	54.4±4.4	38.7±0.5	42.3±1.8	-50.2	-25.7
Mg	4.6±0.05	4.4±0.55	4.1±0.05	4.2±0.20	3.1±0.02	3.7±0.30	-33.5	-16.6
Si	0.4±0.004	0.8±0.05	0.8±0.1	1.2±0.2	1.0±0.04	1.2±0.3†	177.0†	50.0†
Mo	0.23±0.003	0.30±0.01	0.18±0.001	0.24±0.03	0.13±0.001	0.19±0.05	-43.5	-36.7
Al	0.035±0.004	1.9±3.7	0.054±0.006	0.042±0.003	0.074±0.001	0.053±0.01	110.0	-97.2
Mn	0.06±0.001	0.5±0.1	0.05±0.001	0.3±0.1	0.06±0.004	0.2±0.2	0.0	-60.0
Ni	0.03±0.001	0.07±0.004	0.02±0.001	0.05±0.01	0.03±0.0	0.04±0.01	0.0	-45.1
Fe	0.02±0.003	0.02±0.01	0.03±0.004	0.01±0.005	0.05±0.001	0.03±0.01	150.0	50.0
Zn	0.0043±0.0012	0.0155±0.011	0.0067±0.0029	0.0098±0.0027	0.0065±0.0021	0.0079±0.0013	51.1	-48.4
NO_3	35.6±0.1	23.1±1.0	27.1±0.4	23.4±4.2	14.4±0.8	14.5±1.8	-59.6	-37.3
NH_4	5.5±0.1	2.9±0.1	0.9±0.01	0.8±0.1	2.13±0.0	1.8±0.1	-61.4	-36.6

Appendix C

Frank Lake CE-QUAL-W2 Model Development - Detailed Methods

Bathymetry, Topography and Model Grid Development

Advanced software (Burlison UnderSee Explorer version 2.7.1.0) and hardware (Lowrance GPS/Depth sounder) were used to obtain and electronic .SLG data file of updated bathymetry on Lim and Frank Lakes in August and October 2013 respectively. The software has the ability to output volume-area-elevation data, which is critical for model calibration. The hardware simultaneously measured latitude, longitude and depth at a set distance interval (1 and 3m were used) and a computer was used to view the developing bathymetry in UnderSee Explorer. A plot of the tracking routes for Frank Lake can be seen in Figure 2.1. In the UnderSee Explorer software, the Global Adjustment feature was used to set the water surface elevation to a known reference water level. It was ensured that this bathymetry water level was congruent with the HOBO-data logger water level value. In order to input the shoreline into UnderSee Explorer, the lake is viewed in Google Earth and a polygon was carefully developed around the lake and saved as a .KML file. The .KML file wa readily input into UnderSee and surrounded the lake bathymetry dataset. UnderSee automatically gave this shoreline the same elevation as the set water surface. From UnderSee, the bathymetry and shoreline x, y, z coordinates are exported to Microsoft Excel.

Golden Software's SURFER 12 was used to open this Excel file to develop the contour map shown in both Figures 2.1 and 2.2. The coordinate system was set to the Lambert Conformal Conic projection so that the x, y, z data points were all in meters rather than latitude and longitude. In order to incorporate topography data around the bathymetry and shoreline data, a digital elevation model (DEM) dataset was obtained from http://geogratis.gc.ca/site/eng/extraction. The DEM and bathymetry datasets were overlapped in SURFER and the DEM data points present within the lake area were deleted from the dataset.

In order to develop the model grid, a thalweg (deepest flow channel) was drawn for the main channel (branch 1) and bays (branches 2 and 3) for Frank Lake and model segments were built using the thalwegs as a guide.

Using SURFER, each segment was individually "blanked" away from the rest of the map and the volume of each 1m layer elevation within the blanked segment was calculated. Using the calculated volumes, 1m layer heights and the segment lengths, the average width of each grid cell was calculated using a rearrangement of the equation:

Volume = Length x Width x Height

Such that width was the unknown variable:

Width = Volume/(Length x Height)

A code/script written for SURFER's SCRIPTER software was used to aid in this repetitive and iterative calculation process. The reason that an average cell width is calculated is due to the fact that the bottom of lake ecosystems is not square but is actually sloping and irregular and so the volume-calculated width is the best representation of the width of any particular cell. Figure 2.22 illustrates how the width of a cell varies across its height (from top to bottom) and why this premise is employed.

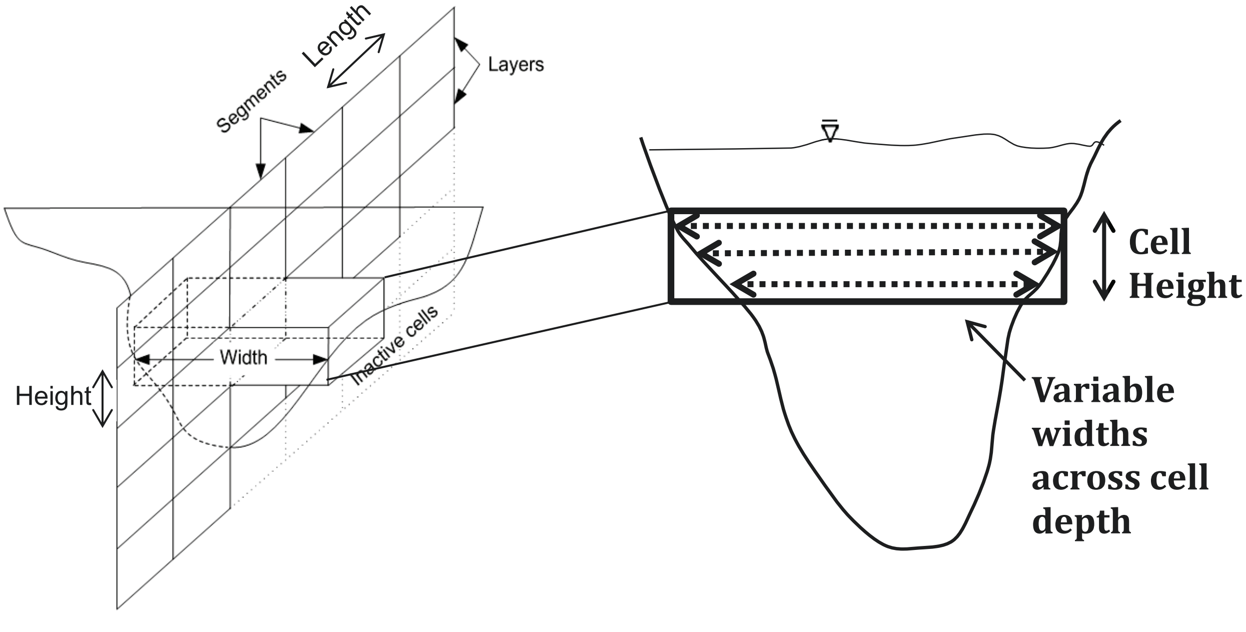


Figure 2.22. Schematic representation of how cell width varies from cell top to bottom, which dictates the need for an average cell width.

Using the average widths and segment directional orientations (radians), the bathymetry input file for the model was developed.

Inflow and Outflow Data

Flow data at the inlet and outlet was obtained using a Swoffer Model 2100 Series Current Meter. The meter measured the amount of rotations of a propeller in a given amount of time and converted those values to ft sec^{-1} values. The methods outlined by the United States Geological Survey (Buchanan and Somers 1976) to measure flow formed the basis of the methods used in the field for this project. Simply, a start bank is chosen on a cross section of stream with few obstructions (rocks, logs etc.) and flow measurements are taken at 12'' – 24'' intervals along the cross section from the start bank to the end bank. Areas of the stream where the depth exceeded 6 inches, flow was taken at the top, middle and bottom of the flow sample location. At each individual flow location, 10-15 flow measurements were taken so a confident average could be calculated. Depth and distance from the start bank were recorded at each location on the cross section. Based on the ft sec^{-1} data and the measured stream dimensions, ft^3 sec^{-1} flow volumes were calculated and converted to m^3 sec^{-1} for the model. The flow meter was calibrated using manufacturer procedure in the lab prior to each field session. Interpolation between the sample sessions of inflows and outflows was used to build temporally-comprehensive model input files.

Inflow and Outflow Temperature and TDS

In order to obtain continuous data for temperature and sp-cond at the in/outlets of Frank Lake, data loggers were deployed. Data loggers utilized for the study included; ONSET HOBO U24's (sp-cond, temperature) and an RBR Global XR-420CTD (sp-cond, temperature, depth). The data loggers were placed in white PVC piping (to prevent solar heating) with holes drilled for adequate water flow and submersed using cinder blocks in the main streams flowing in and out of Frank Lake. All loggers were set to capture data every 30 minutes. Based on the memory and calibration requirements of the logger manufacturers, data was downloaded at various time intervals and the loggers were cleaned of biofouling and re-calibrated. The more precise locations of the data loggers can be viewed in Figure 1.3 in Appendix A.

HOBOware version 3.7.5 and Ruskin version 1.12.1 software programs were utilized to manage the data from their respective loggers. Prior to export, data from these loggers required compensation/manipulation using the Data Compensation Assistants built into the software. Using the Conductivity Assistant, temperature and conductivity were used to calculate sp-cond for each logged datum. A correlation between the lab-analyzed sp-cond and TDS from water samples (Figure 2.23) was used to calculate TDS using the HOBO-measured sp-cond so that a comprehensive TDS data set could be used for model input.

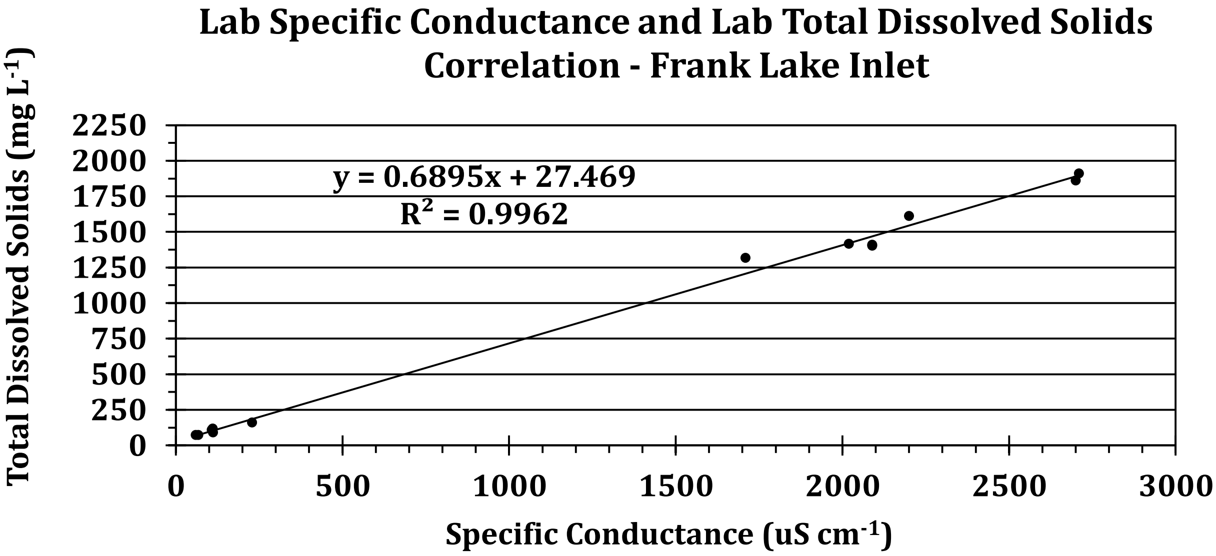


Figure 2.23 Correlation between laboratory-analyzed specific conductance and TDS for development of TDS constituent input file for model.

Water Elevation

An ONSET HOBO U20 (pressure, temperature) logger was placed within Frank Lake using a cinder block and sling apparatus at a depth where they would be safe from ice to measure changes in lake surface elevation throughout 2013. Using the Barometric Compensation Assistant in HOBOware, the pressure measurements (kPa) from the loggers were compensated for barometric pressure and referenced to a known elevation point on the lake. This allowed for conversion of pressure data into water elevation (m) change. Barometric pressure data obtained from Hemlo's meteorological station were used to compensate for any changes in pressure measured by the HOBO water level logger that were attributed to air pressure change rather than actual water level change. Although the water level data was not directly used in the modeling input data, it was utilized to identify discrepancies in water levels predicted by the model and can be used as an input into the W2 Water Balance Utility. This utility creates an inflow file to act as a tributary inflow to compensate for a deficiency in water in the model water balance. As well, a staff gauge was installed on a rock out crop on both lakes to allow for a "real-world double check" of the instrument-logged water level data.

Meteorological Data

A meteorological station measuring data every hour was present within 4.0km of Frank Lake. Data measured by the station included date, time, temperature, dew point temperature, wind speed, wind direction and short-wave solar radiation, all of which were required inputs for the model. Using a variety of calculations, short-wave solar radiation was used to calculate cloud cover, which is on a 1-10 scale in the model, and was also input to the model. Wind sheltering coefficients were set to 0.50 for the segments comprising branch 1 and the segments of branches 2 and 3 that were in proximity to the connection of these branches with branch 1. Otherwise, the segments of branches 2 and 3 were presumed to be more sheltered from the wind and had WSC's of 0.40. All of the segments were given a shade level of 1.0 in the shade file meaning that 100% long-range radiation exposure on the water's surface.

Hydraulic and Kinetic Coefficients

Initially, default coefficients were used however adjustments of multiple coefficients were required to obtain an appropriate model calibration.

Table 2.2. Parameters adjusted in sensitivity analysis.

Parameter	Adjusted Value	Original Value
Wind-Sheltering Coefficient	0.5 and 0.4	0.8 and 0.7
Height of wind measurement from lake	18.4	5
TSED (sediment temperature)	6.0	8.0
BETA (fraction incident solar rad absorbed at surface)	1.0	0.45
EXH2O (light extinction coefficient)	1.0	0.45

Other Model Details

In order to connect the west-bay near the inlet (branch 2) and the east-bay near the outlet (branch 3) to the main channel of Frank Lake (branch 1), an internal head boundary condition was used. Segment 13 in Branch 1 was used as the connection of branch 3 to branch 1 since it was the deepest segment present in the branch (Figures 2.2 and 2.3).

The outflow from Frank Lake occurs through a beaver dam. A variety of outflow structures are able to be modeled in CE-QUAL-W2 however a spillway was utilized for Frank Lake since it was the most accurate representation of this beaver dam. Even though this is not a human-engineered structure, an upstream head (Δh) (water elevation above the spillway crest) vs. flow relationship and equation through the dam was performed since it is required for accurate modeling of outflow (Figure 2.24). The equation for the linear relationship of flow and Δh was used to calculate model coefficients for the structure to suit the spillway equation required by CE-QUAL-W2:

$$\mathbf{Q = \alpha_1 \Delta h^{\beta_1}}$$

Q = flow rate (m^3 sec^{-1})

$\Delta h = Z_u - Z_{sp}$ (masl)

Z_u = upstream head (lake elevation) (masl)

Z_{sp} = spillway crest elevation (masl)

α_1 = empirical coefficient

β_1 = empirical coefficient

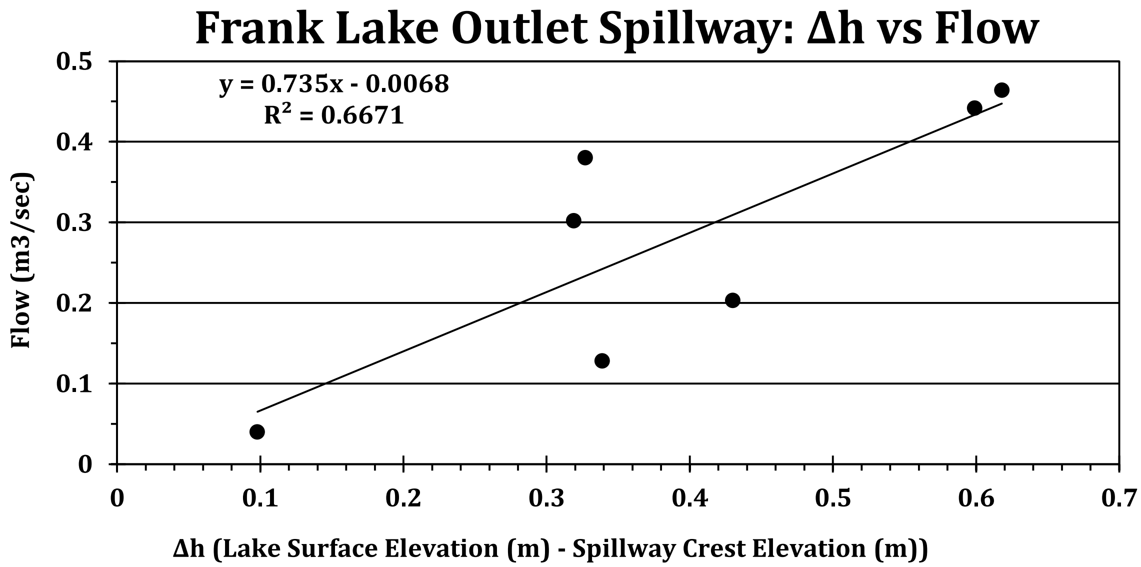


Figure 2.24. Upstream head versus flow relationship for the beaver dam which was represented as a spillway at the outlet of Frank Lake.

Graph File

The graph file is used to manipulate the hydraulic parameters and water quality constituents that wish to be modeled. It is essentially a file that allows the user to specify the format they that they wish outputs to occur in, including output units (mg L^{-1} versus ppt etc.).

Control File

The control file is essentially master file for a particular model as is essentially the dashboard where the "knobs and dials" of the model are adjusted. All aspects of model set-up including hydraulic and kinetic parameters/coefficients, time step controls, model structure properties, input file names and model output preferences. The control file used for Frank Lake can be found below.

Listed below are all of the input files used in the modeling of Frank Lake:

qin_br1.npt, qin_br2.npt, qin_br3.npt – **branch inflow rate files**

tin_br1.npt, tin_br2.npt, tin_br3.npt – **branch inflow temperature files**

cin_br1.npt, cin_br2.npt, cin_br3.npt – **branch inflow constituent files**

qpr_br1.npt, qpr_br2.npt, qpr_br3.npt - **branch precipitation rate files** tpr_br1.npt, tpr_br2.npt, tpr_br3.npt - **branch precipitation temperature files**

cpr_br1.npt, cpr_br2.npt, cpr_br3.npt - **branch precipitation constituent files**

w2_con – **control file**

bath.csv – **waterbody bathymetry file**

met.npt – **waterbody meteorological file**

wsc.npt – **wind-sheltering coefficient file**

shade.npt – **shade coefficient file**

lpr.npt – **longitudinal profile file**

graph.npt – **graph file**

el_obs2013.npt – **observed water elevations file**

calibtempseg6.npt, calibtempseg13.npt, calibtempseg33.npt, calibtempseg48.npt – **temperature calibration files**

calibtdsseg6.npt, calibtdsseg13.npt, calibdsseg33.npt, calibdsseg48.npt – **TDS calibration files**

Frank Lake Control File

W2 Model Version 3.7

```
TITLE C ..............................TITLE..................................
Frank Lake Model 2013, Steven Uchtenhagen Lakehead University
3 branches, 52 Segments, 33 Layers, Flow and Temperature Calibration
Branch 1: main lake channel, Branch 2: in bay, Branch 3: out bay
Simulation Period is 2013 from April 11/13(1130am) to Nov 11/13(12pm)
1 spillway at outlet(DISTR), internal head at BR1 and BR3 connection
FRESH,no tribs,EXO,=1.0,THETA=0.55,Dx=0.0162,AZC=W2,
SPILLDOWN=DISTR


GRID       NWB    NBR    IMX    KMX   NPROC  CLOSEC
1      3     52     33      1     OFF

IN/OUTFL     NTR     NST     NIW     NWD     NGT     NSP     NPI     NPU
0      0      0      0      0      1      0      0

CONSTITU     NGC     NSS     NAL     NEP    NBOD     NMC     NZP
2      0      0      0      0      0      0

MISCELL    NDAY SELECTC HABTATC ENVIRPC AERATEC INITUWL
100    OFF    OFF    OFF    OFF    OFF

TIME CON  TMSTRT   TMEND    YEAR
101.48  316.50    2013

DLT CON      NDT  DLTMIN DLTINTR
1    1.0     ON

DLT DATE    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD    DLTD
101.48  102.00

DLT  MAX    DLTMAX   DLTMAX   DLTMAX   DLTMAX   DLTMAX   DLTMAX   DLTMAX
DLTMAX  DLTMAX
4.00   100.0

DLT FRN    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF    DLTF
0.70000 0.70000

DLT LIMI    VISC    CELC
WB 1         ON      ON

BRANCH G     US     DS     UHS     DHS     UQB     DQB   NLMIN   SLOPE  SLOPEC
```

```
BR1          2     27      0      0      0      0      1 0.00000 0.00000
BR2         30     40      0      4      0      0      1 0.00000 0.00000
BR3         43     51      0     13      0      0      1 0.00000 0.00000

LOCATION    LAT   LONG   EBOT     BS     BE   JBDN
WB 1     48.652  85.840 316.859      1      3      1

INIT CND     T2I   ICEI  WTYPEC   GRIDC
WB 1       -1.0   0.40   FRESH    RECT

CALCULAT    VBC     EBC     MBC     PQC     EVC     PRC
WB 1         ON      ON      ON      ON      ON      ON

DEAD SEA   WINDC    QINC   QOUTC   HEATC
WB 1         ON      ON      ON      ON

INTERPOL   QINIC   DTRIC    HDIC
BR1         ON     OFF      ON
BR2         ON     OFF      ON
BR3         ON     OFF      ON

HEAT EXCH   SLHTC     SROC    RHEVC    METIC   FETCHC      AFW       BFW       CFW
WINDH
WB 1       TERM      ON     OFF      ON     OFF     9.2    0.46     2.0    18.4

ICE COVER   ICEC  SLICEC  ALBEDO     HWI   BETAI  GAMMAI  ICEMIN   ICET2
WB 1         ON  DETAIL    0.25    10.0     0.6    0.07    0.05     3.0

TRANSPOR   SLTRC   THETA
WB 1    QUICKEST 0.55000

HYD COEF     AX      DX    CBHE    TSED      FI   TSEDF   FRICC      Z0
WB 1     0.0162  0.0162     0.3  6.0000    0.01 1.00000   CHEZY   0.001

EDDY VISC    AZC   AZSLC   AZMAX     FBC       E   ARODI STRCKLR BOUNDFR  TKECAL
WB 1         W2     IMP 1.00000       3   9.535   0.431    24.0    10.0     IMP

N STRUC     NSTR DYNELEV
BR 1          0     OFF
BR 2          0     OFF
BR 3          0     OFF

STR INT    STRIC   STRIC   STRIC   STRIC   STRIC   STRIC   STRIC   STRIC   STRIC
BR 1
BR 2
BR 3
```

```
STR TOP     KTSTR    KTSTR    KTSTR    KTSTR    KTSTR    KTSTR    KTSTR    KTSTR
KTSTR
BR 1
BR 2
BR 3

STR BOT     KBSTR    KBSTR    KBSTR    KBSTR    KBSTR    KBSTR    KBSTR    KBSTR
KBSTR
BR 1
BR 2
BR 3

STR SINK   SINKC   SINKC   SINKC   SINKC   SINKC   SINKC   SINKC   SINKC   SINKC
BR 1
BR 2
BR 3

STR ELEV    ESTR    ESTR    ESTR    ESTR    ESTR    ESTR    ESTR    ESTR    ESTR
BR 1
BR 2
BR 3

STR WIDT     WSTR     WSTR     WSTR     WSTR     WSTR     WSTR     WSTR     WSTR
WSTR
BR 1
BR 2
BR 3

PIPES      IUPI    IDPI    EUPI    EDPI     WPI   DLXPI     FPI  FMINPI   WTHLC DYNPIPE


PIPE UP    PUPIC   ETUPI   EBUPI   KTUPI   KBUPI


PIPE DOWN  PDPIC   ETDPI   EBDPI   KTDPI   KBDPI


SPILLWAYS   IUSP    IDSP     ESP    A1SP    B1SP    A2SP    B2SP  LATSPC
SP 1          27       0 344.650   0.735 1.02569   0.735 1.02569    DOWN

SPILL UP   PUSPC   ETUSP   EBUSP   KTUSP   KBUSP
SP 1       DISTR                       2       5

SPILL DOWN PDSPC   ETUSP   EBUSP   KTDSP   KBDSP
SP 1       DISTR                       2       2
```

SPILL GAS GASSPC EQSP ASP BSP CSP
SP 1 OFF

GATES IUGT IDGT EGT A1GT B1GT G1GT A2GT B2GT G2GT LATGTC

GATE WEIR GA1 GB1 GA2 GB2 DYNGC GTIC

GATE UP PUGTC ETUGT EBUGT KTUGT KBUGT

GATE DOWN PDGTC ETDGT EBDGT KTDGT KBDGT

GATE GAS GASGTC EQGT AGASGT BGASGT CGASGT

PUMPS 1 IUPU IDPU EPU STRTPU ENDPU EONPU EOFFPU QPU WTHLC DYNPUMP

PUMPS 2 PPUC ETPU EBPU KTPU KBPU

WEIR SEG IWR IWR IWR IWR IWR IWR IWR IWR IWR

WEIR TOP KTWR KTWR KTWR KTWR KTWR KTWR KTWR KTWR KTWR

WEIR BOT KBWR KBWR KBWR KBWR KBWR KBWR KBWR KBWR KBWR

WD INT WDIC WDIC WDIC WDIC WDIC WDIC WDIC WDIC WDIC

WD SEG IWD IWD IWD IWD IWD IWD IWD IWD IWD

WD ELEV EWD EWD EWD EWD EWD EWD EWD EWD EWD

```
WD TOP     KTWD   KTWD   KTWD   KTWD   KTWD   KTWD   KTWD   KTWD
KTWD


WD BOT     KBWD   KBWD   KBWD   KBWD   KBWD   KBWD   KBWD   KBWD
KBWD


TRIB PLA   PTRC   PTRC   PTRC   PTRC   PTRC   PTRC   PTRC   PTRC   PTRC


TRIB INT   TRIC   TRIC   TRIC   TRIC   TRIC   TRIC   TRIC   TRIC   TRIC


TRIB SEG   ITR    ITR    ITR    ITR    ITR    ITR    ITR    ITR    ITR


TRIB TOP   ELTRT   ELTRT   ELTRT   ELTRT   ELTRT   ELTRT   ELTRT   ELTRT
ELTRT


TRIB BOT   ELTRB   ELTRB   ELTRB   ELTRB   ELTRB   ELTRB   ELTRB   ELTRB
ELTRB


DST TRIB   DTRC   DTRC   DTRC   DTRC   DTRC   DTRC   DTRC   DTRC   DTRC
BR 1       OFF
BR 2       OFF
BR 3       OFF

HYD PRIN  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC  HPRWBC
HPRWBC  HPRWBC
NVIOL      ON
U          ON
W          ON
T          ON
RHO        ON
AZ         ON
SHEAR      ON
ST         ON
SB         ON
ADMX       ON
DM         ON
HDG        ON
ADMZ       ON
```

```
HPG          ON
GRAV         ON

SNP PRINT   SNPC    NSNP   NISNP
WB 1         ON       6      17

SNP DATE    SNPD    SNPD    SNPD    SNPD    SNPD    SNPD    SNPD    SNPD    SNPD
WB 1     101.48  103.50  141.50  162.50  231.50  316.40

SNP FREQ    SNPF    SNPF    SNPF    SNPF    SNPF    SNPF    SNPF    SNPF    SNPF
WB 1      0.050     1.0   500.0   500.0   500.0   500.0

SNP SEG     ISNP    ISNP    ISNP    ISNP    ISNP    ISNP    ISNP    ISNP    ISNP
WB 1          2       6      13      14      15      16      25      26      27
30     33     39     40     43     48     50     51

SCR PRINT   SCRC    NSCR
WB 1         ON       2

SCR DATE    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD    SCRD
WB 1     101.48   102.0

SCR FREQ    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF    SCRF
WB 1       0.05    0.25

PRF PLOT    PRFC    NPRF   NIPRF
WB 1         ON       5      17

PRF DATE    PRFD    PRFD    PRFD    PRFD    PRFD    PRFD    PRFD    PRFD    PRFD
WB 1     101.48  141.50  162.50  231.50  316.40

PRF FREQ    PRFF    PRFF    PRFF    PRFF    PRFF    PRFF    PRFF    PRFF    PRFF
WB 1      500.0   500.0   500.0   500.0   500.0

PRF SEG     IPRF    IPRF    IPRF    IPRF    IPRF    IPRF    IPRF    IPRF    IPRF
WB 1          2       6      13      14      15      16      25      26      27
30     33     39     40     43     48     50     51

SPR PLOT    SPRC    NSPR   NISPR
WB 1         ON       5      17

SPR DATE    SPRD    SPRD    SPRD    SPRD    SPRD    SPRD    SPRD    SPRD    SPRD
WB 1     101.48  141.50  162.50  231.50  316.40

SPR FREQ    SPRF    SPRF    SPRF    SPRF    SPRF    SPRF    SPRF    SPRF    SPRF
WB 1      500.0   500.0   500.0   500.0   500.0
```

```
SPR SEG    ISPR   ISPR   ISPR   ISPR   ISPR   ISPR   ISPR   ISPR   ISPR
WB 1        2     6     13     14     15     16     25     26     27
30     33     39     40     43     48     50     51

VPL PLOT    VPLC    NVPL
WB 1        ON      1

VPL DATE    VPLD    VPLD    VPLD    VPLD    VPLD    VPLD    VPLD    VPLD    VPLD
WB 1     101.48

VPL FREQ    VPLF    VPLF    VPLF    VPLF    VPLF    VPLF    VPLF    VPLF    VPLF
WB 1       1.0

CPL PLOT    CPLC    NCPL TECPLOT
WB 1        ON      1    OFF

CPL DATE    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD    CPLD
WB 1     101.48

CPL FREQ    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF    CPLF
WB 1      1.00

FLUXES     FLXC    NFLX
WB 1       OFF      0

FLX DATE    FLXD    FLXD    FLXD    FLXD    FLXD    FLXD    FLXD    FLXD    FLXD
WB 1

FLX FREQ    FLXF    FLXF    FLXF    FLXF    FLXF    FLXF    FLXF    FLXF    FLXF
WB 1

TSR PLOT    TSRC    NTSR   NITSR
ON      1      7

TSR DATE    TSRD    TSRD    TSRD    TSRD    TSRD    TSRD    TSRD    TSRD    TSRD
101.48

TSR FREQ    TSRF    TSRF    TSRF    TSRF    TSRF    TSRF    TSRF    TSRF    TSRF
0.04

TSR SEG    ITSR    ITSR    ITSR    ITSR    ITSR    ITSR    ITSR    ITSR    ITSR
2     6     13     27     33     48     51

TSR LAYE    ETSR    ETSR    ETSR    ETSR    ETSR    ETSR    ETSR    ETSR    ETSR
0.0     0.0
```

```
WITH OUT    WDOC    NWDO   NIWDO
OFF       1       1

WITH DAT    WDOD    WDOD    WDOD    WDOD    WDOD    WDOD    WDOD    WDOD
WDOD
101.48

WITH FRE    WDOF    WDOF    WDOF    WDOF    WDOF    WDOF    WDOF    WDOF
WDOF
7

WITH SEG    IWDO    IWDO    IWDO    IWDO    IWDO    IWDO    IWDO    IWDO    IWDO
27

RESTART     RSOC    NRSO    RSIC
OFF

RSO DATE    RSOD    RSOD    RSOD    RSOD    RSOD    RSOD    RSOD    RSOD    RSOD


RSO FREQ    RSOF    RSOF    RSOF    RSOF    RSOF    RSOF    RSOF    RSOF    RSOF


CST COMP     CCC    LIMC     CUF
ON     OFF       1

CST ACTIVE   CAC
TDS          ON
GENERIC# 1    ON
GENERIC# 2    ON
PO4         OFF
NNH4-N      OFF
NO3-N       OFF
DSI-SI      OFF
PSI-SI      OFF
FE          OFF
LDOM        OFF
RDOM        OFF
LPOM        OFF
RPOM        OFF
DO          OFF
TIC-C       OFF
ALK AS CaCO3 OFF
LDOM-P      OFF
RDOM-P      OFF
```

```
LPOM-P      OFF
RPOM-P      OFF
LDOM-N      OFF
RDOM-N      OFF
LPOM-N      OFF
RPOM-N      OFF

CST DERI   CDWBC   CDWBC   CDWBC   CDWBC   CDWBC   CDWBC   CDWBC   CDWBC
CDWBC
DOC         OFF
POC         OFF
TOC         OFF
DON         OFF
PON         OFF
TON         OFF
TKN         OFF
TN          OFF
DOP         OFF
POP         OFF
TOP         OFF
TP          OFF
APR         OFF
CHLA        OFF
ATOT        OFF
%DO         OFF
TSS         OFF
TISS        OFF
CBOD        OFF
pH          OFF
CO2         OFF
HCO3        OFF
CO3         OFF

CST FLUX   CFWBC   CFWBC   CFWBC   CFWBC   CFWBC   CFWBC   CFWBC   CFWBC
CFWBC
TISSIN      OFF
TISSOUT     OFF
PO4AR       OFF
PO4AG       OFF
PO4AP       OFF
PO4ER       OFF
PO4EG       OFF
PO4EP       OFF
PO4POM      OFF
PO4DOM      OFF
PO4OM       OFF
```

PO4SED	OFF
PO4SOD	OFF
PO4SET	OFF
NH4NITR	OFF
NH4AR	OFF
NH4AG	OFF
NH4AP	OFF
NH4ER	OFF
NH4EG	OFF
NH4EP	OFF
NH4POM	OFF
NH4DOM	OFF
NH4OM	OFF
NH4SED	OFF
NH4SOD	OFF
NO3DEN	OFF
NO3AG	OFF
NO3EG	OFF
NO3SED	OFF
DSIAG	OFF
DSIEG	OFF
DSIPIS	OFF
DSISED	OFF
DSISOD	OFF
DSISET	OFF
PSIAM	OFF
PSINET	OFF
PSIDK	OFF
FESET	OFF
FESED	OFF
LDOMDK	OFF
LRDOM	OFF
RDOMDK	OFF
LDOMAP	OFF
LDOMEP	OFF
LPOMDK	OFF
LRPOM	OFF
RPOMDK	OFF
LPOMAP	OFF
LPOMEP	OFF
LPOMSET	OFF
RPOMSET	OFF
CBODDK	OFF
DOAP	OFF
DOAR	OFF
DOEP	OFF

```
DOER       OFF
DOPOM      OFF
DODOM      OFF
DOOM       OFF
DONITR     OFF
DOCBOD     OFF
DOREAR     OFF
DOSED      OFF
DOSOD      OFF
TICAG      OFF
TICEG      OFF
SEDDK      OFF
SEDAS      OFF
SEDLPOM    OFF
SEDSET     OFF
SODDK      OFF

CST ICON   C2IWB   C2IWB   C2IWB   C2IWB   C2IWB   C2IWB   C2IWB   C2IWB
C2IWB
TDS        -1.0
GENERIC# 1   0.0
GENERIC# 2 100.0
PO4        -1.0
NNH4-N     -1.0
NO3-N      -1.0
DSI-SI     -1.0
PSI-SI     -1.0
FE         -1.0
LDOM       -1.0
RDOM       -1.0
LPOM       -1.0
RPOM       -1.0
DO         -1.0
TIC-C      -1.0
ALK        -1.0
LDOM-P     -1.0
RDOM-P     -1.0
LPOM-P     -1.0
RPOM-P     -1.0
LDOM-N     -1.0
RDOM-N     -1.0
LPOM-N     -1.0
RPOM-N     -1.0

CST PRIN   CPRWBC   CPRWBC   CPRWBC   CPRWBC   CPRWBC   CPRWBC   CPRWBC
CPRWBC  CPRWBC
```

```
TDS          ON
GENERIC# 1    ON
GENERIC# 2    ON
PO4         OFF
NNH4-N      OFF
NO3-N       OFF
DSI-SI      OFF
PSI-SI      OFF
FE          OFF
LDOM        OFF
RDOM        OFF
LPOM        OFF
RPOM        OFF
DO          OFF
TIC-C       OFF
ALK AS CaCO3 OFF
LDOM-P      OFF
RDOM-P      OFF
LPOM-P      OFF
RPOM-P      OFF
LDOM-N      OFF
RDOM-N      OFF
LPOM-N      OFF
RPOM-N      OFF

CIN CON   CINBRC  CINBRC  CINBRC  CINBRC  CINBRC  CINBRC  CINBRC  CINBRC
CINBRC
TDS          ON     ON     ON
GENERIC# 1    ON     ON     ON
GENERIC# 2    ON     ON     ON
PO4         OFF    OFF    OFF
NNH4-N      OFF    OFF    OFF
NO3-N       OFF    OFF    OFF
DSI-SI      OFF    OFF    OFF
PSI-SI      OFF    OFF    OFF
FE          OFF    OFF    OFF
LDOM        OFF    OFF    OFF
RDOM        OFF    OFF    OFF
LPOM        OFF    OFF    OFF
RPOM        OFF    OFF    OFF
DO          OFF    OFF    OFF
TIC-C       OFF    OFF    OFF
ALK AS CaCO3 OFF    OFF    OFF
LDOM-P      OFF    OFF    OFF
RDOM-P      OFF    OFF    OFF
LPOM-P      OFF    OFF    OFF
```

```
RPOM-P      OFF    OFF    OFF
LDOM-N      OFF    OFF    OFF
RDOM-N      OFF    OFF    OFF
LPOM-N      OFF    OFF    OFF
RPOM-N      OFF    OFF    OFF

CTR  CON    CTRTRC   CTRTRC   CTRTRC   CTRTRC   CTRTRC   CTRTRC   CTRTRC
CTRTRC  CTRTRC
TDS         OFF    OFF    OFF
GENERIC# 1   OFF    OFF    OFF
GENERIC# 2   OFF    OFF    OFF
PO4         OFF    OFF    OFF
NNH4-N      OFF    OFF    OFF
NO3-N       OFF    OFF    OFF
DSI-SI      OFF    OFF    OFF
PSI-SI      OFF    OFF    OFF
FE         OFF    OFF    OFF
LDOM        OFF    OFF    OFF
RDOM        OFF    OFF    OFF
LPOM        OFF    OFF    OFF
RPOM        OFF    OFF    OFF
DO          OFF    OFF    OFF
TIC-C       OFF    OFF    OFF
ALK AS CaCO3 OFF    OFF    OFF
LDOM-P      OFF    OFF    OFF
RDOM-P      OFF    OFF    OFF
LPOM-P      OFF    OFF    OFF
RPOM-P      OFF    OFF    OFF
LDOM-N      OFF    OFF    OFF
RDOM-N      OFF    OFF    OFF
LPOM-N      OFF    OFF    OFF
RPOM-N      OFF    OFF    OFF

CDT  CON    CDTBRC   CDTBRC   CDTBRC   CDTBRC   CDTBRC   CDTBRC   CDTBRC
CDTBRC  CDTBRC
TDS         OFF    OFF    OFF
GENERIC# 1   OFF    OFF    OFF
GENERIC# 2   OFF    OFF    OFF
PO4         OFF    OFF    OFF
NNH4-N      OFF    OFF    OFF
NO3-N       OFF    OFF    OFF
DSI-SI      OFF    OFF    OFF
PSI-SI      OFF    OFF    OFF
FE         OFF    OFF    OFF
LDOM        OFF    OFF    OFF
RDOM        OFF    OFF    OFF
```

```
LPOM        OFF    OFF    OFF
RPOM        OFF    OFF    OFF
DO         OFF    OFF    OFF
TIC-C       OFF    OFF    OFF
ALK AS CaCO3 OFF    OFF    OFF
LDOM-P      OFF    OFF    OFF
RDOM-P      OFF    OFF    OFF
LPOM-P      OFF    OFF    OFF
RPOM-P      OFF    OFF    OFF
LDOM-N      OFF    OFF    OFF
RDOM-N      OFF    OFF    OFF
LPOM-N      OFF    OFF    OFF
RPOM-N      OFF    OFF    OFF

CPR CON   CPRBRC  CPRBRC  CPRBRC  CPRBRC  CPRBRC  CPRBRC  CPRBRC  CPRBRC
CPRBRC
TDS         ON     ON     ON
GENERIC# 1   ON     ON     ON
GENERIC# 2   ON     ON     ON
PO4         OFF    OFF    OFF
NNH4-N      OFF    OFF    OFF
NO3-N       OFF    OFF    OFF
DSI-SI      OFF    OFF    OFF
PSI-SI      OFF    OFF    OFF
FE         OFF    OFF    OFF
LDOM        OFF    OFF    OFF
RDOM        OFF    OFF    OFF
LPOM        OFF    OFF    OFF
RPOM        OFF    OFF    OFF
DO         OFF    OFF    OFF
TIC-C       OFF    OFF    OFF
ALK AS CaCO3 OFF    OFF    OFF
LDOM-P      OFF    OFF    OFF
RDOM-P      OFF    OFF    OFF
LPOM-P      OFF    OFF    OFF
RPOM-P      OFF    OFF    OFF
LDOM-N      OFF    OFF    OFF
RDOM-N      OFF    OFF    OFF
LPOM-N      OFF    OFF    OFF
RPOM-N      OFF    OFF    OFF

EX COEF    EXH2O    EXSS    EXOM    BETA    EXC    EXIC
WB 1       1.00     0.1     0.1    1.00     OFF     OFF

ALG EX      EXA    EXA    EXA    EXA    EXA    EXA    EXA    EXA    EXA
Wb 1       0.20
```

```
ZOO EX      EXZ     EXZ     EXZ     EXZ     EXZ     EXZ
0.20

MACRO EX    EXM     EXM     EXM     EXM     EXM     EXM
0.0100

GENERIC    CGQ10   CG0DK   CG1DK     CGS
CG 1     0.00000 0.00000 0.00000 0.00000
CG 2     0.00000 -1.0000 0.00000 0.00000

S SOLIDS     SSS   SEDRC   TAUCR
SS# 1    1.00000     OFF    1.00

ALGAL RATE    AG      AR      AE      AM      AS    AHSP    AHSN   AHSSI    ASAT
ALG1         2.00000  0.04000  0.04000    0.1000    0.1000  0.00300  0.01400  0.00000
100.000

ALGAL TEMP   AT1     AT2     AT3     AT4     AK1     AK2     AK3     AK4
ALG1     5.00000 25.0000 35.0000 40.0000 0.10000 0.99000 0.99000 0.10000

ALG STOI    ALGP    ALGN    ALGC   ALGSI   ACHLA   ALPOM   ANEQN    ANPR
ALG1     0.00500 0.08000 0.45000    0.18    0.05 0.80000       2 0.00100

EPIPHYTE    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC    EPIC
EPI1        OFF

EPI PRIN    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC    EPRC
EPI1        OFF

EPI INIT   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI   EPICI
EPI1     0.00000

EPI RATE      EG      ER      EE      EM      ES    EHSP    EHSN   EHSSI
EPI1     2.00000 0.04000 0.04000 0.10000   0.001   0.003   0.014 0.00000

EPI HALF    ESAT     EHS   ENEQN    ENPR
EPI1      75.000 35.0000       2   0.001

EPI TEMP     ET1     ET2     ET3     ET4     EK1     EK2     EK3     EK4
EPI1     5.00000 25.0000 35.0000 40.0000 0.10000 0.99000 0.99000 0.10000

EPI STOI      EP      EN      EC     ESI   ECHLA    EPOM
EPI1      0.0005    0.08    0.45  0.0018    0.05    0.80

ZOOP RATE     ZG      ZR      ZM    ZEFF   PREFP  ZOOMIN    ZS2P
```

```
Zoo1      1.50   0.10   0.01   0.50   0.50   0.01    0.3

ZOOP ALGP   PREFA    PREFA    PREFA    PREFA    PREFA    PREFA    PREFA    PREFA
PREFA
Zoo1      0.5

ZOOP ZOOP   PREFZ    PREFZ    PREFZ    PREFZ    PREFZ    PREFZ    PREFZ    PREFZ
PREFZ
Zoo1      0.00

ZOOP TEMP    ZT1    ZT2    ZT3    ZT4    ZK1    ZK2    ZK3    ZK4
5.0   25.0   35.0   40.0    0.1   0.99   0.99  0.100

ZOOP STOI    ZP     ZN     ZC
0.00500 0.08000 0.45000

MACROPHY    MACWBC    MACWBC    MACWBC    MACWBC    MACWBC    MACWBC
MACWBC  MACWBC  MACWBC
Mac1       OFF

MAC  PRINT    MPRWBC    MPRWBC    MPRWBC    MPRWBC    MPRWBC    MPRWBC
MPRWBC  MPRWBC  MPRWBC
Mac1       OFF

MAC   INI     MACWBCI   MACWBCI   MACWBCI   MACWBCI   MACWBCI   MACWBCI
MACWBCI MACWBCI MACWBCI
Mac1    0.00000

MAC RATE     MG     MR     MM    MSAT    MHSP    MHSN    MHSC    MPOM  LRPMAC
Mac 1      0.30   0.05   0.05   30.0    0.0     0.0     0.0     0.9     0.2

MAC SED     PSED    NSED
MAC 1       1.0     1.0

MAC DIST    MBMP    MMAX
Mac 1      40.0   500.0

MAC DRAG  CDDRAG    DMV    DWSA   ANORM
Mac 1       2.0 7.0E+04    8.0     0.3

MAC TEMP     MT1     MT2     MT3     MT4     MK1     MK2     MK3     MK4
Mac 1       5.0    25.0    35.0    40.0     0.1    0.99    0.99     0.1

MAC STOICH    MP      MN      MC
Mac 1     0.005    0.08    0.45
```

```
DOM       LDOMDK  RDOMDK   LRDDK
WB 1        0.1   0.001    0.01

POM       LPOMDK  RPOMDK   LRPDK    POMS
WB 1       0.08   0.001    0.01     0.1

OM STOIC    ORGP    ORGN    ORGC   ORGSI
WB 1      0.005    0.08    0.45    0.18

OM RATE     OMT1    OMT2    OMK1    OMK2
WB 1     4.00000 25.0000  0.1000 0.99000

CBOD       KBOD    TBOD     RBOD   CBODS
BOD 1       0.1    1.02     1.85     0.0

CBOD STOIC  BODP    BODN    BODC
BOD 1      0.004    0.06    0.32

PHOSPHOR    PO4R   PARTP
WB 1      0.001 0.00000

AMMONIUM    NH4R   NH4DK
WB 1      0.001    0.12

NH4 RATE   NH4T1   NH4T2   NH4K1   NH4K2
Wb 1      5.000  25.000   0.100   0.990

NITRATE    NO3DK    NO3S FNO3SED
WB 1       0.03   0.001    0.00

NO3 RATE   NO3T1   NO3T2   NO3K1   NO3K2
Wb 1      5.000  25.000   0.100   0.990

SILICA      DSIR    PSIS   PSIDK  PARTSI
WB 1     0.10000  1.0000 0.30000 0.20000

IRON         FER     FES
WB 1         0.5     2.0

SED CO2     CO2R
WB 1         1.2

STOICH 1   O2NH4    O2OM
WB 1        4.57     1.4

STOICH 2    O2AR    O2AG
```

```
ALG1     1.10000 1.40000

STOICH 3    O2ER    O2EG
EPI1     1.10000 1.40000

STOICH 4    O2ZR
ZOO1     1.10000

STOICH 5    O2MR    O2MG
MAC1        1.1     1.4

O2 LIMIT   O2LIM
0.7

SEDIMENT    SEDC  SEDPRC   SEDCI    SEDK    SEDS    FSOD    FSED    SEDB DYNSEDK
WB 1        OFF     OFF 0.00000     0.1     0.1 1.00000 1.00000    0.01     OFF

SOD RATE   SODT1   SODT2   SODK1   SODK2
Wb 1       4.000  25.000   0.100   0.990

S DEMAND     SOD     SOD     SOD     SOD     SOD     SOD     SOD     SOD     SOD
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000

REAERATION  TYPE    EQN#   COEF1   COEF2   COEF3   COEF4
WB 1        LAKE       6 0.00000 0.00000 0.00000 0.00000

RSI FILE..................................RSIFN.................................
rsi.npt - not used

QWD FILE..................................QWDFN.................................
qwd.npt - not used

QGT FILE..................................QGTFN.................................
qgt.npt - not used

WSC FILE..................................WSCFN.................................
wscexp.npt

SHD FILE..................................SHDFN.................................
shade.npt
```

BTH FILE..................................BTHFN.................................
WB 1   bath_frank.csv

MET FILE..................................METFN.................................
WB 1   met2013 (working).npt

EXT FILE..................................EXTFN.................................
WB 1   ext_1.npt - not used

VPR FILE..................................VPRFN.................................
WB 1   vpr_br1.npt

LPR FILE..................................LPRFN.................................
WB 1   lpr_april2013free5.npt - not used

QIN FILE..................................QINFN.................................
BR 1   qin_br1.npt
BR 2   qin_br2.npt
BR 3   qin_br3.npt

TIN FILE..................................TINFN.................................
BR 1   tin_br1.npt
BR 2   tin_br2.npt
BR 3   tin_br3.npt

CIN FILE..................................CINFN.................................
BR 1   cin_br1.npt
BR 2   cin_br2.npt
BR 3   cin_br3.npt

QOT FILE..................................QOTFN.................................
BR 1   qot_br1.npt
BR 2   qot_br2.npt - not used
BR 3   qot_br3.npt - not used

QTR FILE..................................QTRFN.................................
TR1   qtr_tr1.npt - not used

TTR FILE..................................TTRFN.................................
TR1   qtr_tr1.npt - not used

CTR FILE..................................CTRFN.................................
TR1   ctr_tr1.npt - not used

QDT FILE..................................QDTFN.................................
BR1   qdt_tr1.npt - not used

BR1 qdt_tr2.npt - not used
BR1 qdt_tr3.npt - not used

TDT FILE..................................TDTFN.................................
BR1 tdt_tr1.npt - not used
BR1 tdt_tr2.npt - not used
BR1 tdt_tr3.npt - not used

CDT FILE..................................CDTFN.................................
BR1 cdt_tr1.npt - not used
BR2 cdt_tr2.npt - not used
BR3 cdt_tr3.npt - not used

PRE FILE..................................PREFN.................................
BR1 qpr_br1.npt
BR2 qpr_br2.npt
BR3 qpr_br3.npt

TPR FILE..................................TPRFN.................................
BR1 tpr_br1.npt
BR2 tpr_br2.npt
BR3 tpr_br3.npt

CPR FILE..................................CPRFN.................................
BR1 cpr_br1.npt
BR2 cpr_br2.npt
BR3 cpr_br3.npt

EUH FILE..................................EUHFN.................................
BR1 euh_br1.npt - not used
BR2 euh_br2.npt - not used
BR3 euh_br3.npt - not used

TUH FILE..................................TUHFN.................................
BR1 tuh_br1.npt - not used
BR2 tuh_br2.npt - not used
BR3 tuh_br3.npt - not used

CUH FILE..................................CUHFN.................................
BR1 cuh_br1.npt - not used
BR2 cuh_br2.npt - not used
BR3 cuh_br3.npt - not used

EDH FILE..................................EDHFN.................................
BR1 edh_br1.npt - not used
BR2 edh_br2.npt - not used

BR3 edh_br3.npt - not used

TDH FILE.................................TDHFN................................
BR1 tdh_br1.npt - not used
BR2 tdh_br2.npt - not used
BR3 tdh_br3.npt - not used

CDH FILE.................................CDHFN................................
BR1 cdh_br1.npt - not used
BR2 cdh_br2.npt - not used
BR3 cdh_br3.npt - not used

SNP FILE.................................SNPFN................................
WB 1 snp.opt

PRF FILE.................................PRFFN................................
WB 1 prf.opt

VPL FILE.................................VPLFN................................
WB 1 vpl.w2l

CPL FILE.................................CPLFN................................
WB 1 cpl.opt

SPR FILE.................................SPRFN................................
WB 1 spr.opt

FLX FILE.................................FLXFN................................
WB 1 flx.opt - not used

TSR FILE.................................TSRFN................................
tsr.opt - not used

WDO FILE.................................WDOFN................................
wdo.opt