The Influence of Wetlands and Watershed Geology on Lake Chemistry of Five Remote Lakes in Northwestern Ontario

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Abstract

In chapter 1 of this study the relationship between spatial, chemical, and biological factors and their influence on mercury concentrations in walleye were examined. Water, sediment, and fish tissue samples were collected in the summer of the 2008 from 5 lakes near Aroland First Nation, in Nortwesthern, Ontario, Canada and analyzed for metals, mercury, pH, and alkalinity. Arc GIS was used to extract spatial data from base maps and digital elevation models, in order to calculate lake area, watershed area, and wetland area for each study lake. Hg concentrations in fish tissue were compared between lakes using a standardized length using an ANCOVA. The test proved that a significant difference was present ($p=0.0000$ with 95% confidence intervals). Walleye (Sander vitreum) from Melchett Lake had the highest levels of mercury with a mean concentration of 0,5505ug/g, while Esnagami had the lowest at 0.2228 ug/g.

A nonparametric Kruskal-Wallis ANOVA compared ranks of concentrations of chemical variables associated with Hg, between lakes. Melchett Lake statistically ranked the highest in DOC concentrations and lowest in alkalinity and pH (second lowest). Esangami ranked lowest in DOC concentrations, and highest for alkalinity and pH, suggesting that a high DOC concentration and low alkalinity in Melchett Lake helped increase mercury concentrations within fish.

A backward stepwise multiple regression was performed on all biological, chemical and spatial data to isolate variables that contribute most to Hg concentration in Walleye from the entire study area. Wetland area ($\beta=6.439$), fish length ($\beta=0.559$), watershed area ($\beta=-5.797$), and % wetlands ($\beta=-1.26$) were significant predictors of Hg in fish tissue.

Hg concentrations in Walleye from the Aroland First Nations appear to be dependent on a complex interaction of factors, in particular DOC, pH, alkalinity, wetland abundance and fish length. Although growth rates were not calculated they play an important role on Hg levels in fish from northern remote lakes and should be considered in future studies.

In chapter 2 the role of geology on water chemistry and mercury concentrations in 5 lakes in Northwestern Ontario, Canada was evaluated. Water and rock samples were collected from 5 study lakes near Aroland First Nation in the summer of 2008. Water samples were analyzed for metals, pH, alkalinity, and mercury, while X-Ray diffraction analysis was performed on rocks samples to distinguish mineralization content. Remaining rock was used in a water/rock interaction column experiment to evaluate chemical weathering and leaching.

A discriminant function analysis was used to separate lakes by their lake chemical signatures. Alkalinity, potassium and sulphur were used as functions in the final analysis to separate lakes. Water chemistry was also compared by lake using a Kruskal-Wallis ANOVA. Results were then compared to XRD data and column experiment results. Lakes (Esnagami) containing the mineral dolomite ranked highest in alkalinity and Ca concentrations. Furthermore lakes such as Melchett and Briarcliff with an abundance of K bearing minerals, had some of the highest amounts of K in both lake water chemistry and column experiments. Finally O'Sullivan Lake had abundant Fe and Al bearing minerals within its surrounding watershed. Fe and Al concentrations were highest in O'Sullivan Lake.

Thus while surrounding geology contributes small amounts of mercury to aquatic systems in the Aroland region, it is negligible when compared to the amount contributed by wetlands.

Geochemistry influenced water chemistry in lakes from the Aroland region. In particular the abundant micas and feldspars contribute significant amounts of K, Fe, and Al. Furthermore lakes with carbonate minerals had higher levels of alkalinity and Ca.

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General Introduction

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General Introduction

Aroland first nation is situated in the heart of the boreal forest, approximately 350km northeast of Thunder Bay, Ontario, and 90 km north of Geraldton, Ontario. The area lies within the arctic watershed surrounded by a diverse geological and geographic landscape. The community of Aroland is able to access traditional lands for hunting, fishing, and gathering of local food, to maintain a healthy well being for the people of the community. This study forms part of larger project entitled "Assessment of mercury and heavy metal contaminant concentrations in humans and food sources (fish blueberries, grouse, and wild rice) and effects on health and socio-cultural traditions: A risk management strategy and guideline for traditional food consumption. The project was proposed by the Aroland First Nation in partnership with Lakehead University and Health Canada as a continuation of a university student's thesis, which found that elevated levels of mercury in Walleye from lakes commonly used by the community.

For this study, six lakes were chosen based on their importance to the Aroland community as food sources, and the presence of the fish species walleye *(Sander vitreum).* Walleye was chosen as the fish species because it is an important food source to the community of Aroland and a popular recreational species to anglers. Melchett, O'Sullivan, Chaucer, Esnagami and Briarcliff lakes (Fig. 1.0) were chosen for the study since they are commonly used by the residents of Aroland. It was known the lakes differed in geology, surrounding vegetation, and land use. A description of lake location (UTM coordinates) and surface area of each study lake is displayed in Table 1.0.

Figure 1.0. Aerial photo from Google Earth displaying study lakes

Table 1.0. Description of lake coordinates and surface area for Aroland study lakes

Study Lake	*UTM (N)*	*UTM (E)*	*Surface Area (km^2)*
Melchett	499588	5618067	14.7
O'Sullivan	496782	5584922	42.06
Chaucer	499689	5612606	1.57
Briarcliff	502917	5615670	1.27
Esnagami	509801	5574845	68.18

Geological Setting of Lake Watersheds

Esnagami Lake

Esnagami Lake is situated in two distinct geological boundaries. The majority of the rock surrounding the north, west, and northeast portions of the lake are situated in the Esnagami Batholith. The rock in this area is of Neoarchean age (2700-2799 Ma) and consists of granodiorite to tonalite bearing biotite with quartz phenocrysts. Various age phases of the batholith contain both unmetamorphosed to weakly deformed fractures containing chlorite and epidote. The southeast portion of the lake is situated in the Eastern Wabigoon Subprovince which is of neoarchean age (2700-2799 Ma). The lithology in this region of lake consists of tonalite to granodiorite gneiss gneiss. Fine to medium grained gneiss with late granite dikes and amphibolite inclusions can be found east of Onaman Lake to Nakina, and north of Longlac (Stott, et al, 2002).

O'Sullivan Lake

Three distinct geological areas are adjacent to O'sullivan Lake. The east and west shores of the lake are situated within the Willet assemblage, and is composed of pillowed theoletic basalt. Trace element geochemical characteristics are consistent with either a back-arc basin or a mix of ocean floor and lesser primitive island arc affinities. Particular lithologies in the O'sullivan Lake area include metavolcanic rocks (ca, 2740 Ma) consisting of fine grained, nonvesicular massive to pillowed flows.

Throughout the area of O'Sullivan Lake are Neoarchan diabase intrusive gabbro rock gabbroic rocks (gabbro to leucogabbro) (Stott, et al. 2002). A small portion of southeast O'Sullivan Lake is adjacent to the Esnagami batholith, which was previously described in the Esnagami Lake section.

Melchett Lake

Melchett Lake is situated within two distinct geological boundaries. The majority of Melchett Lake is surrounded by Archean aged metasediments consisting of conglomerate, quartzite, greywacke, akrose, slate, mica schist and tuff. Archean basic and intermediate metavolcanics rocks include; greenstone, basalt, pillow lava, metadiabase, andesite, dacite, amphibolite, chlorite schist, and hornblende schist (Pye, et al, 1965).

Briarcliff Lake

Briarcliff Lake is situated entirely in Archean aged metasediments. This geological unit was previously described in the geological settings of Melchett Lake.

Chaucer Lake

Chaucer Lake is situated entirely in Archean aged metasediments. This geological unit was previously described in the geological settings of Melchett Lake.

Mercury in the Aquatic Environment

Mercury is one of the most studied trace metals due to its toxic nature and unique ability to bioaccumulate in the environment, (Morel et al. 1998). Mercury is a transition metal, but unlike other metals, mercury is a liquid at room temperature and is fairly volatile due to its relatively high vapour pressure (Stein et al,1996).

Once consumed, methylmercury is quickly absorbed by the gastrointestinal tract where it is distributed to tissues throughout the body (Clarkson, 1997). Exposure to mercury causes a wide array of effects on humans. Depending on the exposure time and dosage, effects are both chronic and acute. Exposure to high levels in both short and long time periods can lead to severe neurological disorders. Early symptoms are blurred vision, parathesia, malaise, which can lead to ataxia, deafness, and dysarthria, Exposure to very high concentrations can lead to coma and death (Health Canada, 2007).

Symptoms due to long-term low exposure are much more subtle. Studies from eastern Finland have found that high mercury content in men, is correlated to high incidence of coronary and cardiovascular disease (Loukala-Ruskeniemi et al, 2003).

Recently mercury exposure to pregnant women has drawn major concern from health organizations around the world. Research shows that methylmercury can interfere with proper neurological development of fetuses and infants. Thus the World Health Organization developed a recommended daily intake of 0.71ug Hg/kg body wt./day (based on a 60 kilogram adult), with no more then two thirds being methylmercury. It is recommended that pregnant women and infants are subjected to no more then 1.6ug Hg/kg body wt./week (Health Canada, 2007).

Mercury enters the environment in a variety of ways. Three main sources in which mercury may enter natural surface waters and lakes are through atmospheric deposition, weathering of rock bearing mercury, and release from wetlands (in particular peatlands) (Rudd, 1995)(Rasmussen et al 1998).

Since the onset of the industrial revolution anthropogenic processes drastically increased the concentration of mercury in the environment (Scheuhammer and Graham, 1999). Although point sources of mercury have been significantly reduced atmospheric concentrations are steadily rising due to the burning of fossil fuels. Total global mercury emissions during the mid 1990s were approximately 1900-2000 tonnes per year (Pacyna and Pacyna, 2001). Researchers now believe that anthropogenic sources equal or exceed that of natural sources of mercury (Scheuhammer and Graham, 1999). This theory is sufficiently supported by studies from core samples of lake sediments in Northern Canada, which show a doubling of mercury deposition over the past 50 years (Lockhart et al. 1998).

Of the estimated 1900 tonnes of mercury released into the atmosphere, approximately 90-95% is in an inorganic form (either elemental Hg^0 53% or the gaseous bivalent form, where it is then slowly oxidized by ozone and other oxidants to its mercuric state Hg (II) (Morel et al, 1998).

Slow oxidation rates give mercury a significant resident time in the atmosphere (approximately 27 years) (Morel et al, 1998). Over time it moves throughout the atmosphere in a phenomena known as long-range atmospheric transport (LRAT). LRAT is responsible for introducing contaminants to remote areas of the world thousands of miles away from any anthropogenic source. This results in the presence of heavy metals in the arctic (Hermanson and Brozokski, 2005).

Mercury is transported back to the Earth's surface mostly in the form of wet deposition, and to a lesser extent aerosols and particulate matter. The annual atmospheric deposition of mercury to remote unpolluted areas (similar to the Aroland region) is $3ug/m^2/yr$, of which 70-90% is in a complexed mercuric form (Hg(II), 1-10% is in the elemental form (Hg^0), and 1-20% is in an organic methyl form (MeHg)(Morel et al. 1998).

Although the origin of MeHg in atmospheric deposition is debatable, remote areas of Northwestern Ontario receive approximately 0.39 mg/ha/yr, some of the lowest recorded levels found in the northern hemisphere (Rudd, 1995).

Upon entering an aquatic system, a complex system of cycling and chemical transformation occurs. Dissolved mercury is distributed over several forms throughout the water column, Hg^o is fairly un-reactive and is generally found in higher concentrations near the water surface-air interface due to its volatility (Ullrich et al, 2001). Several forms of the divalent Hg(II) also exist as hydroxide and chloride (in the absence of sulphide) complexes. The presence and availability of these complexes are dependent on pH and chloride concentrations of the lake (Hahne and Kroontje, 1973).

The third species of mercury found in natural waters occurs as organic complexes. Organic mercury complexes are found in two forms; dimethyl mercury species, which is unreactive, and the monomethyl species, which is commonly found bound to organic particles, and to a lesser extent as chloro and hydroxide complexes (Morel et al, 1998; Lindvquist, 1991).

As previously mentioned of all the species of mercury present in a lacustrine system at one time monomethyl mercury is the one of greatest concern. Although only a small fraction of mercury deposited from the atmosphere is in the methyl form, methylation of inorganic mercury can occur within the lake sediment and to a lesser extent in the water column (Winfrey and Rudd, 1990). Methylmercury produced within organic soils and wetlands in lake catchments also contribute to in lake Hg levels (Heyes, et al, 2000). The majority of in lake mercury methylation occurs in anaerobic sediments, at the redox boundary. This usually coincides with the sediment-water interface, (although some methylation occurs within the water column) It is then distributed within the lake by diffusion and advection. (Rudd et al,1983; Winfrey and Rudd, 1990).

Methylmercury is believed to be produced by a group of anaerobic sulphate reducing bacteria (SRB),(although some facultative anaerobes and aerobes have also shown to be capable of methylation) (Compeau and Bartha, 1985). Methylation rates are therefore highest in anaerobic conditions, and decrease with increasing oxygen due to reduced activity by the SRB. The efficiency and rate at which microbes are able to produce MeHg depend mainly on microbial activity, and the concentration of available Hg for the microbes (Ullrich et al, 2001). These in turn are also influenced by temperature, pH, and concentration of inorganic and organic complexing agents and redox conditions (Langley, 1973).

Generally the highest rates of methylation occur in summer when water temperatures are moderately warm. This increases microbial activity (Korthals and Winfrey, 1987). MeHg released from sediments was 50 to 70 % higher when water temperatures were 20°C compared to that of winter temperatures of 4°C (Wright and Hamilton, 1982). Likewise demethylation rates favour lower temperatures, and thus methylmercury concentrations are reduced during winter months (Ullrich et al, 2001).

There is a negative correlation between Hg levels in fish tissue and decreasing lake pH (Miskimmin et al, 1992). Many theories have suggested explanations for these correlations. Likely methylation rates increase with a reduction in pH. Studies indicate that a drop in pH from 7 to 5 increased MeHg production by 100-200%. The increase of MeHg at pH 5-7 has been attributed to a shift in the production of dimethylmercury to monomethylmercury, which is less volatile and thus more available to bioaccumualtion (Winfrey and Rudd, 1990).

Acidic conditions also increase the solubility and mobility of Hg and MeHg as well as other metals, thus mercury concentrations can be pH dependent. Therefore a drop in pH can increase in Hg inputs from the watershed into the lake (Lee and Hultberg, 1990). Reduced pH values in lakes are often associated with Acid Mine Drainage, which typically have high concentrations of sulphate. The addition of sulphate increases the microbial activity of the sulphur reducing bacteria associated with increasing mercury methylation (Suchanek et al, 2000).

Higher concentrations of dissolved organic carbon (DOC) are closely associated with higher levels of mercury in lake water, sediments and fish tissue (Ullrich et al, 2001). Strong correlations occur between mercury concentrations in perch, and pike and lake water-colour. Water colour serves as an indicator of the amount of organic matter (particularly humic substances) within a lake (Nillsson and Hakanson, 1992). However the exact role of DOC and other organic matter is in this process is unclear. DOC may act as a nutrient for methylating microbes increasing their productivity. This in turn produces more methyl mercury (Ullrich, et al, 2001). The most supported theory suggests that organic matter does not play a part in producing MeHg but rather is used to transport MeHg that is produced within the watershed, such as that from a wetland or peatland (Heyes et al, 2000).

Watershed Characteristics: Area of Wetlands in Upland Areas and Their Inputs of DOC and Mercury to Receiving Lakes using ArcGIS

1.0 Introduction

Mercury concentrations in fish of remote boreal lakes are a result of numerous complex interactions between chemical, biological, and environmental (or spatial) factors. Each and every aquatic system has a unique and specific combination of interactions among these factors, making Hg concentrations highly variable through space and time (Simoneau, et al, 2005).

Numerous biological factors influence Hg concentrations in fish. Because methyl mercury bioaccumulates in the aquatic environment, Hg concentrations in fish generally increase with length and age (Evans et al, 2005). Mercury also biomagnifies in the environment, thus an increase in trophic position is associated with higher Hg levels. Predatory fish such as walleye will generally have higher levels of mercury then herbivorous fish of the same size (Greenfield et al, 2001).

Fish growth rates play an important role in regulating Hg levels. Slow growing fish typically have higher levels of Hg in their tissue compared to that of a fast growing fish of the same size. This phenomenon has been termed "biodilution", as it refers to the overall reduction of a contaminant due to accelerated growth resulting from differences in bioenergetic processes (Simoneau, et al, 2005; Lavigne, et al. 2010).

Numerous environmental and spatial factors present within a lakes watershed influence Hg concentrations in fish populations. These factors include the area of wetland within the watershed, watershed size, lake size. (Gabriel et al, 2009;Garcia and Carignan, 2000).

Wetlands, and in particular peatlands, are large producers of methyl mercury. Wetlands retain the majority of atmospherically deposited mercury and typically provide favourable conditions for MeHg production (acidic, anoxic, high organic content)(Watras et al, 2005). Remote wetlands receive most of their mercury from atmospheric deposition. Hg becomes trapped and complexed with organic material in the top layer of soil, and then methylated by sulphate-reducing bacteria (Nilsson and Hakanson, 1992). The release of organic and humic material allows the MeHg to be transported within the watershed, and then deposited into receiving lakes and streams within the watershed as dissolved organic carbon (DOC). Factors such as high rainfall, surface run off, and human activities such as drainage of wetlands promotes the release and transport of organic material, and thus play a large role in MeHg deposition into lakes (Watras et al. 2005)(Nilsson and Hakanson, 1992).

Studies performed in the Experimental Lakes Area (ELA) in Northwestern, Ontario show that streams with upland and headwater areas containing wetlands and peatlands consistently had higher levels of MeHg then streams with no wetlands in their headwater/upland reaches. Furthermore catchments containing higher wetland abundances by percent and area consistently display higher levels of mercury (Rudd, 1995; Watras et al, 2005, Greenfield et al, 2001).

Catchment size and the amount of disturbance within the catchment also affect Hg concentrations. Larger catchments are typically associated with higher levels of mercury, as is disturbance. Activities such as logging or forest fires disrupt the natural cycling of Hg in watersheds and release Hg into the aquatic system, thereby increasing Hg in aquatic biota (Garcia and Carignan, 2000, Garcia et al, 2007).

Lake size is another important factor influencing Hg concentrations in fish. Bodaly et al. (1993) found an inverse relationship between lake and mercury concentration in fish in remote Canadian Shield lakes. Higher mercury concentrations in fish from smaller lakes are due to higher epilimnetic water temperatures. Smaller lakes, warming earlier in the spring, have higher midsummer temperatures. This enhances microbial mercury methylation (Bodaly et al, 1993). Methylation of mercury is more predominant in deeper lakes. Deeper lakes have a larger area of hypolimnion, during summer stratification. Hence much of the in lake mercury methylation likely occurs in the hypolimnion, due to anoxic conditions, common in this strata (Nilsson and Hakanson, 1992).

A number of chemical factors also influence mercury concentrations in fish. Dissolved organic carbon (previously explained), pH, alkalinity, and sulphide have all been associated with Hg.

There is a negative correlation between Hg levels in fish tissue and decreasing lake pH. Methylation rates do increase with a reduction in pH. Thus a drop in pH from 7 to 5 results in a 100-200% increase in MeHg production. The increase of MeHg at pH 5-7 results from a shift in the production of dimethylmercury to monomethylmercury,. The latter is less volatile and thus more available to bioaccumualtion (Winfrey and Rudd, 1990).

Closely associated to lake pH, is alkalinity. Alkalinity is the buffering capability of a lake or the ability to withstand changes in pH (Wetzel, 2001). Aquatic biotas in lakes with low alkalinity typically have higher concentrations of Hg compared to lakes with high alkalinity. This is impart due to increased rates of methylation by sulphate reducing bacteria and the greater in take of dietary available Hg within the system (Weiner et al, 1990; Lathrop et al, 1991)

Sulphate levels are also correlated with elevated mercury concentrations. The addition of sulphate increases the microbial activity of the sulphur reducing bacteria that are associated with mercury methylation, resulting in higher levels of methylmercury (Suchanek et al, 2000; Branfireun, et al, 1999).

Geographical Information Systems (GIS), are recognized by environmental mangers as a powerful and cost effective tool in the manipulation and interpretation of hydrological data pertaining to water quality (Luzio et al, 2004). With the use of high-resolution digital elevation models (DEM), GIS software can extract drainage information, such as flow direction, and watershed delineations (Turcotte, et al, 2001).

All of the above factors are influential in any one specific geographical area. This paper examines the biological, environmental, and chemical factors and their impact on Hg concentrations in water, sediment, and Walleye from lakes in Northwestern Ontario. Spatial characteristics and in particular wetland abundance within the lakes catchment areas and their influences on Hg levels will be the focus of this paper. Lakes that received inputs from upland catchments with large areas of wetlands should display statistically higher levels of dissolved and organic carbon. If so this will result in higher levels of mercury in lake water, sediments, and aquatic biota.

1.1 Methods

1.1.1 GIS Watershed Manipulation Procedure

Arc GIS 9.3 was used to examine watershed characteristics of each of the study lakes. Ontario base maps and digital elevation models of the study area were acquired from Lakehead University's Patterson Library. The digital elevation model was filled and checked for sinks or areas of low relief. Flow direction was calculated followed by flow accumulation. A conditional statement with the flow accumulation input was used, until a accumulation value was met that paired well to the base map of the river systems. A watershed map was produced using the stream link function in the ArcGIS watershed tool. This was done using the flow direction as the input to develop a stream network. Pourpoints were calculated based on values found from the flow direction.

Next a 300 meter buffer was created around each of the study lakes and any watershed that was included within the buffer was included into each study lakes analysis. A total of 5 watersheds were produced (one for each study lake). From the final output the area of each watershed was calculated. NTS map data was used to overlay wetlands situated in each watershed. The area of wetland in each watershed was also calculated, as well as % wetland in each watershed.

1.1.2 Study Site and Fish Sampling

Fish were collected from the study lakes in the summer of 2008, by angling. Angling was requested by the community of Aroland as the collection method for fish samples. A guideline of 10 fish from each study lake was used following the same protocol used by Gassel et al, 2005 in a similar study. Angling allowed some fish to be released with minimal damage if needed be, whereas more invasive methods such as gill nets increase the chance of injury or mortality to the fish.

Walleye (*Sander vitreum*) a popular sport fish and food source was chosen as the target species, This fish is a top predator in most lakes therefore will have higher accumulation of mercury compared to fish in lower tropic levels (Kidd, et al 1995).

All walleye kept for tissue analysis were measured (mm) and weighed (g) immediately after being caught. The fish were then filleted (skin removed) and a small piece of flesh approximately 10-30 grams was removed above the lateral line, anterior to the dorsal fin from the left side of the fish. The liver from each walleye was also removed and weighed. Both liver and flesh were separately wrapped in aluminum foil and placed in Ziploc bags and immediately frozen until analysis at LUEL. To reduce the chance of contamination strict quality control measures were followed. Powder free latex rubber gloves were used (and changed for every fish) at all times during the handling of the fish. All knives and cutting boards were rinsed with a dilute 2% HCl solution and double distilled water (DDW) between each fish.

1.1.3 Water and Sediment Sampling

Ten water samples were taken using a Kemmerer bottle in the summer of 2008 from each lake. Sampling sites were chosen at random, and were distributed throughout each lake to ensure all regions of the lakes were represented in analysis. At each site a sample from both the surface and bottom was taken and put into a 1 liter polyethylene bottles (HDPE #2), and kept cool, until laboratory analysis. To ensure quality control one field duplicate was taken at a site in each lake. Field duplicates are used to ensure proper field sampling techniques were used, and were used to identify variations among samples caused by sampling errors.

Separate water samples were taken at each of the sites for mercury analysis. Mercury is a trace metal and therefore extreme precaution must be taken as samples are easily contaminated, resulting in erroneous data. Water samples for mercury analysis were collected following the United States Environmental Protection Agency’s protocol:

"Sampling Ambient Water for Trace Metals- Method 1669" in which a "clean hands" "dirty hands" sampling procedure was employed to reduce the chance of contamination.

Water samples taken for mercury analysis were collected using an inert Kemmerer bottle made for collection of trace metals. Samples were collected using EPAs "clean hands, dirty hands" collection method for trace metals, and placed into a 500mL borosilicate bottle. Samples were preserved with 4mL/L of pre-tested 11.6 M HCl and refridgerated until time of analysis at LUEL.

Sediment was also collected at each site using a Eckman dredge. Collected sediments were then placed into a plastic Ziploc bag where they were kept cool (or frozen) until analysis at LUEL.

1.1.4 Laboratory Procedure for Fish Tissue Analysis

Fish samples were mechanically liquefied in the lab in which a 10mL aliquot was taken analyzed for metals using ICP (see metals in water analysis). The rest of the sample was treated with BrCl and analyzed for mercury content using BrooksRAnd, following the EPA's method 1631 digestion II protocol.

1.1.5 Laboratory Procedure for Water and Sediment Analysis

Water samples were analyzed at the Lakehead University Environmental Laboratory (LUEL), in Thunder Bay, Ontario, for metals, pH, conductivity, dissolved organic carbon, and total alkalinity. LUEL is an ISO17025 accredited environmental laboratory, which follows a strict quality assurance/quality control protocol. For each test a blank consisting of double deionized water (DDW) was analyzed, followed by a standardized QC samples. Furthermore a randomly selected sample was analyzed twice as the laboratory repeat.

Analysis of water samples closely followed a standardized operating procedure (SOP) specific to the method being used for each parameter. SOPs were adapted by LUEL staff from the Standard Methods for the Examination of Water and Wastewater 18th ed. for pH/Alkalinity/Conductivity

pH, alkalinity, and conductivity was measured on unfiltered samples at room temperature. Both pH and alkalinity were measured simultaneously using a DL53 Mettler titrator, and a DL20 autosampler with the software LabX Lite version 1.1.

Conductivity was measured using the Accumet XL60 multi meter with an Accumet conductivity probe. To ensure accuracy a temperature compensation probe was used during conductivity analysis.

Metals

Samples analyzed for metal content were prepared at LUEL by digesting samples with nitric acid and concentrating them to five times that of pre-concentration using microwave. Samples were then analyzed at Lakehead University's Instrumentation Laboratory, using inductively coupled atomic emission spectrometry (ICP-AES). ICP-AES measures element-specific characteristic emission spectra produced by a radio frequency inductively coupled plasma by optical spectrometry.

Dissolved Organic Carbon

Samples were first filtered through a 0.45μm filter. A known volume of the filtered sample was then injected into a hear reaction vessel, in which the water is vapourized and organic carbon is oxidized in carbon dioxide and water. CO_2 was then transported in a carrier gas stream and measured by a nondispersive infrared analyzer, giving the total organic carbon present in the sample.

Laboratory procedures for mercury analysis of water followed EPA's method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapour Atomic Fluorescence Spectromery.

Sediment

A 10mL aliquot of sediment was taken and analyzed for metals using ICP-AES. (see water for procedure). The rest of the sediment sample was then used for mercury analysis following EPA's method 1631, digestion II

1.1.6 Procedure for Statistical Analysis

Data analysis proceeded in 5 steps:

(i) In order to assess if a significant difference in mercury concentration in fish STATISTICA 7.0 was used to explore descriptive statistics of both biological (fish lengths and weights) and chemical data (Hg concentrations in fish) for each study area. The Kolmogorov-Smirnov and Lilliefors tests were used to assess the normality of the data. Parameters that did not follow a normal distribution were log transformed in order to pass tests for normality.

(ii) Fish length and size are typically positively correlated with Hg concentration in fish tissue. To see if the data from the Aroland study lakes followed the same pattern a simple linear regression was performed using STATISTICA 7.0. Because simple linear regressions require normally distributed variables, the log-transformed data was used.

(iii) Because length and size are considered a continuous predictor of mercury concentration in fish tissue an analysis of covariance (ANCOVA) was performed using the STATISTICA software program. ANCOVA's have the ability to assess the effects of the categorical predictor (lake) on a dependent variable (Hg concentration in fish tissue) after accounting for the effects of one or more independent covariates (fish length) (Hill and Lewicki, 2006). There are three assumptions for an ANCOVA; i) a normally distributed dependent variable (which has been fulfilled by the log transformation of the data), ii) data are sampled randomly, and iii) homogeneity of slope. Therefore STATISTICA was used to test the homogeneity of slope between fish mercury concentration between lakes.

(iv) A Kruskal-Wallis ANOVA was used to determine if any significant differences were present among chemical variables that may influence Hg levels found in Walleye between lakes. Dissolved organic carbon, pH, sulphur, iron, alkalinity, Hg in sediment, and Hg in water, were all analyzed for significant differences between lakes. Water chemistry data did not follow a normal distribution and thus did not follow the assumptions required for an ANOVA. The Kruskal-Wallis ANOVA is a non-parametric test used to assess the hypothesis that the different samples in the comparison were drawn from the same distribution or from distributions with the same median (Hill, and Lewicki, 2006). Interpretation of the Kruskal-Wallis is similar to that of the ANOVA, except that results are based on equality of ranks rather then means between groups. (Hill and Lewicki, 2006).

(v) A backward stepwise multiple regression was performed using the STATISICA software package on biological, spatial, and chemical variables that have been shown to affect mercury concentrations in aquatic environments. A backward stepwise multiple regression begins by examining the combined effects of all independent or predictor variables on the dependent variables (Hg concentration in fish tissue). In each step the weakest predictor variable is removed (the variable with the highest P value) and the analysis is performed again. This procedure is repeated until all remaining variables have an individual P value that is less then the accepted P value.

Prior to the multiple regression all variables were assessed for multicollinearity using a pairwise correlation matrix. Any data that was significantly correlated was removed from the multiple regression analysis.

1.2 Results

1.2.1 Results from GIS Manipulation

Geographic information systems were used to extract spatial data regarding watershed traits for each study lake; including watershed area, lake area, area of wetlands, and % wetlands in watershed. The results from this analysis are illustrated in Table 1.1. ArcGIS also produces detailed output of the results. Found in the output is a map displaying the study lakes and their corresponding watershed boundaries and wetlands contained within each watershed (Figure 1.1).

Table 1.1. Summary of results from GIS analysis of spatial data from Aroland study lakes Table illustrates areas of watershed, lake, wetland abundance, and % wetlands for each lakes

Lake	Watershed Area(km^2)	Lake Area (km^2)	Area of Wetlands in Watershed (km^2)	% Wetlands in Watershed
Melchett	155.92	14.7	8.53	5.47
Briarcliff	369.32	1.27	17.48	4.73
Chaucer	18.95	1.57	0.36	1.9
O'Sullivan	187.77	42.06	13.86	7.38
Esnagami	248.16	68.18	10.86	4.37

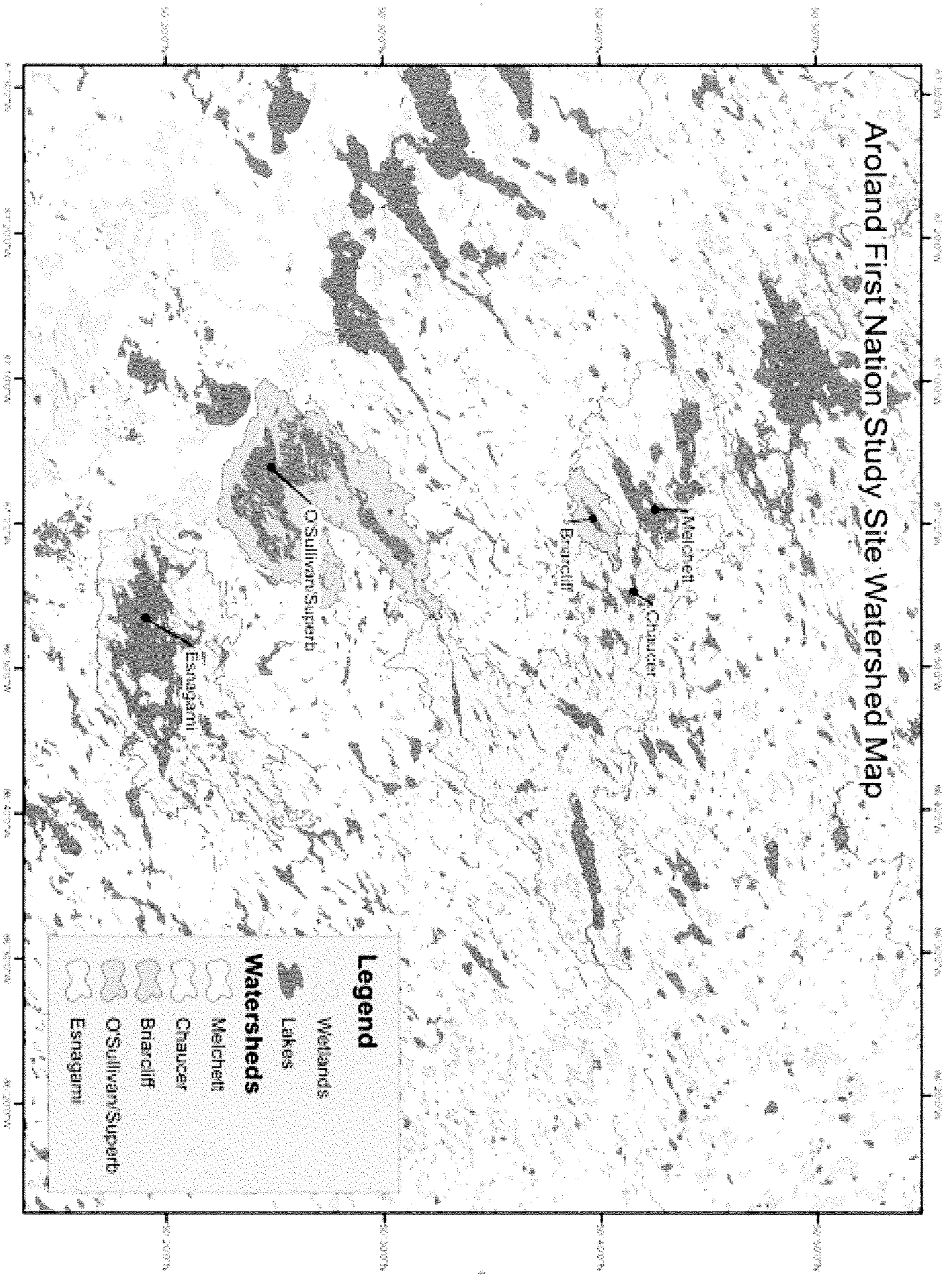

Figure 1.1. Map displaying delineated watersheds and wetlands of lakes from the Aroland study area

1.2.2 Descriptive Statistics

Descriptive statistics were used to explore the biological data of the Walleye caught from the study area. Table 1.2 shows the mean and standard deviation of fish length, fish weight, and mercury concentration in fish tissue for each lake. The Kolmogorov-Smirnov and Lilliefors tests for normality were also performed as part of descriptive statistics for fish length and mercury concentration. The distributions for both fish length and mercury did not follow a normal distribution. Untransformed data of mercury concentration from fish tissue had a p value > 0.2, and a Lilliefors correction of p value > 0.5, suggesting the data did not follow a normal distribution. Fish length data and mercury concentration in fish tissue data were log transformed for a more acceptable distribution. After log transformation fish length data had a p-value of >0.2 and a Lillifors correction of <0.05, which is considered a normal distribution. Log transformed Hg concentration in fish had a p-value of >0.2 and a Lilliefors correction value of p>0.20. This is statistically considered a normal distribution.

Table 1.2. Summary of means and standard deviations of fish lengths, weights, and Hg concentrations

Lake	Fish Len. (mm)	Fish Wt. (g)	Hg Conc. (ug/g)
Melchett (N=8)	389.75 +/- 65.42	727.88 +/- 289.16	0.5505 +/- 0.1516
Briarcliff (N=9)	389.33 +/- 49.03	575.81 +/- 268.29	0.2460 +/- 0.0994
Esnagami (N=10)	421.00 +/- 43.79	680.39 +/- 219.29	0.2228 +/- 0.0902
Chaucer (N=5)	371.67 +/- 50.11	510.29 +/- 232.40	0.3926 +/- 0.3497
Osullivan (N=12)	345.00 +/- 31.34	374.45 +/- 127.28	0.3748 +/- 0.0939

1.2.3 ANCOVA

Literature illustrates that a positive correlation between fish size (length) and mercury concentration in fish tissue exists (Evans et al. 2005, Lathrop et al 1991). Linear regressions were used to analyze fish length data vs. Hg concentrations separately for each lake.

A positive correlation was found to exist for all lakes except Chaucer, suggesting that length is a covariate of Hg concentration in fish. Thus an ANCOVA is considered an appropriate test to be used rather then an ANOVA. Tests of slope homogeneity for log mercury concentration vs. log fish length for each lake indicate results of F= 0.19 and p= 0.94. This indicates that the slope of log Hg concentrations vs. log fish length the same for all lakes (treatments).

Results of the ANCOVA can be found in Figure 1.2. The graph shows the mean and standard deviations for the log transformed mercury concentrations in fish tissue. The test standardized fish length for all lakes to log 5.94, which is equivalent to 379.93mm. Final results of the ANCOVA were found to have an F-value of 16.52 in which p= 0.000. This indicates that a significant statistical difference is present in Walleye mercury concentrations between study lakes when length is statistically controlled. Table 1.2 illustrates that Walleye from Melchett Lake had the highest levels of mercury, while Esnagami and Briarcliff had the lowest.

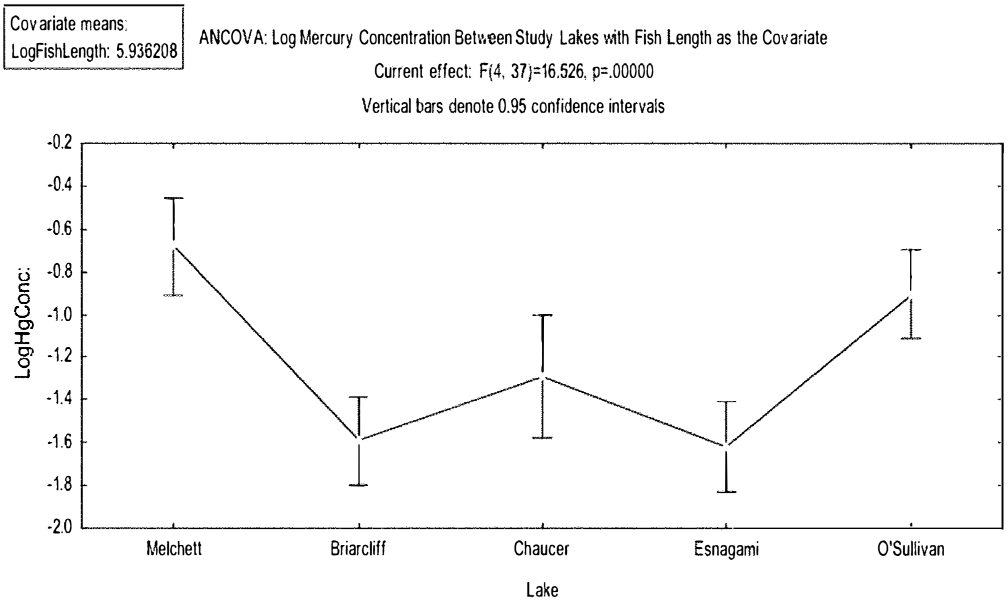

Figure 1.2. Graph showing mean and standard deviations for log transformed Hg concentration in fish tissue for standardized log fish length 5.937 (380mm). Also shown on graph is results from ANCOVA test

1.2.4 Comparison of Water Chemistry Between Lakes

Water chemistry was analyzed for total metals, alkalinity, total mercury and dissolved organic carbon. Mean concentrations of each the parameters are illustrated in Table 1.3. Melchett Lake was found to have the highest concentrations of DOC (11.34 ppm) and the lowest concentration of alkalinity (50.62 ppm). Esnagami Lake on the other hand had the highest levels of alkalinity (80.7ppm) and lowest levels of dissolved organic carbon (6.41 ppm). pH levels throughout each were circum-neutral, and varied between 7.2 (Briarcliff) and 7.67 (Esngami). Total mercury concentrations in water and sediment were also measured. Melchett Lake was found to have the highest mean levels in both water and sediment with average concentrations of 3.23ppb and 0.1ppm respectively. Esnagami had the lowest mercury levels within the lake water at 0.07ppb.

Table 1.3. Mean concentrations of Total Metal, Alkalinity, DOC, pH, and total Hg in water and sediment for each of the study lakes

Chemical Parameter	Melchett	Briarcliff	Chaucer	O'Sullivan	Esnagami
Total Alkalinity as CaCO3 (ppm)	50.62	51.46	67.76	77.14	80.7
Dissolved Organic Carbon (ppm_	11.34	10.46	10.1	10.37	6.41
Total Aluminum (ppm)	0.0136	0.03	0.02	0.04	0.02
Total Barium (ppm)	0.0068	0.01	0.001	0.001	0.01
Total Calcium (ppm)	15.96	16.34	21.05	25.2	25.18
Total Iron (ppm)	0.08	0.12	0.09	0.11	0.04
Total Potassium (ppm)	0.64	0.66	0.6	0.6	0.6
Total Magnesium (ppm)	3.26	3.35	4.17	4.66	4.8
Total Manganese (ppm)	0.01	0.01	0.01	0.002	0.01
Total Sodium (ppm)	0.51	0.54	0.61	0.69	0.69
Total Sulfur (ppm)	0.36	0.34	0.32	0.44	0.43
Total Strontium (ppm)	0.02	0.02	0.02	0.02	0.02
pH	7.48	7.2	7.64	7.57	7.67
Total Hg in Water (ppb)	3.23	4.8	2.2	2.98	0.93
Total Hg in Sediment (ppb)	0.1	0.04	0.07	0.1	0.07

A Kruskal-Wallis ANOVA was used to evaluate if the differences found in chemical concentrations between each lake was statistically significant by comparing ranks based on medians. The ranks of alkalinity, pH, iron, sulphur, DOC, Hg in water, and Hg in sediment were all tested for significant differences. A summary of the results from Kruskal-Wallis ANOVA can be found in Table 1.4. Melchett Lake, which had the highest levels of mercury in Walleye, was found to have significantly higher rank of dissolved organic carbon, and the lowest rank of alkalinity. Melchett also ranked second lowest in comparisons of pH. Esnagami Lake which was found to have the lowest mercury concentrations in Walleye, ranked significantly lower in DOC and iron. Furthermore Esnagami ranked significantly higher in pH and alkalinity. The test also illustrated that there was no significant difference among ranks between lakes for total mercury concentrations in water and sediment samples.

Table 1.4. Results from the Kruskal-Wallis ANOVA comparison of ranks between water and sediment parameters, where H= the kruskal wallis statisic (approximation of the Chi-squared distribution)(R= ordinal rank of concentration, and p=significnance <0.05

DOC	Kruskal-Wallis test: H_4=27.19, **p =.0000**				
	OSullivan	Briar	Esna	Chauc	Melchett
	R:31.464	R:32.864	R:5.650	R:27.650	R:40.500
Alkalinity	Kruskal-Wallis test: H_4=46.72, **p =.0000**				
	OSullivan	Briar	Esna	Chauc	Melchett
	R:40.429	R:12.273	R:47.800	R:26.500	R:9.6000
Iron	Kruskal-Wallis test: H_4=11.38 **p =.0246**				
	OSullivan	Briar	Esna	Chauc	Melchett
	R:27.929	R:35.045	R:13.600	R:32.350	R:30.400
Total Mercury H_2O	Kruskal-Wallis test: H_4= 4.28 p =.3692				
	Osullivan	Briarc	Esna	Chauc	Melchett
	R:15.375	R:7.2500	R:12.500	R:16.500	R:11.688
pH	Kruskal-Wallis test: H_4= 35.62, **p =.0000**				
	OSullivan	Briar	Esna	Chauc	Melchett
	R:31.286	R:6.0000	R:42.400	R:40.200	R:21.000
Sulfur	Kruskal-Wallis test: H_4=46.08, **p =.0000**				
	OSullivan	Briar	Esna	Chauc	Melchett
	R:43.857	R:16.227	R:43.000	R:6.7500	R:25.000
Mercury in Sed.	Kruskal-Wallis test: H_4= 7.50, p =.1118				
	Osullivan	Briar	Esna	Chauc	Melchett
	R:17.571	R:6.8000	R:11.333	R:11.000	R:15.800

1.2.5 Stepwise Multiple Regression

In order to examine what biological, spatial, and chemical parameters were influencing mercury concentrations in Walleye from the Aroland study area a backward stepwise multiple regression was used. All parameters used in the multiple regression have been found in previous literature to influence mercury concentrations in aquatic environments both positively and negatively. A pairwise correlation was performed to test for multicollinearity within the variables. Variables that are highly correlated cause redundancy, which will affect the multiple regression model. Thus redundant predictor variables must be isolated and removed from the multiple regression analysis. Results from the pairwise correlation found length and weight were highly correlated with an R-value=0.91. Calcium and alkalinity were also highly correlated (R=0.99). Weight and calcium were removed from the multiple regression analysis to avoid redundancy. A backward stepwise regression was then performed using the log transformed mercury concentration in fish tissue as the dependent variable. Length, watershed area lake area, wetlands area, % wetlands in watershed, alkalinity, dissolved organic carbon, pH, iron, and sulphur were used as the predictor variables. Fish length, watershed area, wetlands area, and % wetlands in watershed were the most statistically significant variables influencing mercury concentration in fish in the Aroland study area. Beta results suggest whether the variables are positively or negatively correlated with mercury concentration. Length (<0.01, $\beta=0.559$) and wetland area ($p<0.01$, $\beta=6.439$) were positively correlated with mercury concentration in fish tissue, whereas watershed area ($p=<0.01$ β-5.797) and % wetlands ($p<0.01$, $\beta= -1.526$) was negatively correlated with mercury concentration in fish tissue. The entire model had an R-value = 0.810, F- value= 19.141, and p-value= 0.00.

1.3 Discussion

1.3.1 Mercury Levels in Fish Tissue

Mercury levels in fish tissue have long been recognized as a threat to human health. The Ontario Ministry of the Environment has published restrictions for mercury consumption in the Ontario Guide to Eating Sport Fish. Consumption restrictions begin at 0.26ppm with total consumption restrictions being advised for levels greater then

0.52ppm. These guidelines are based on toxicological data developed by Health Canada, which accounts for intake from all environmental pathways (air, water, and food) (OMOE, 2010). Although results from this study are presented as total mercury estimates have shown that methylmercury in fish tissue accounts for 80 to anywhere up to 100% of the total mercury content found in fish tissue (Kannan et al 2008).

When length was standardized Melchett Lake was statistically found to have the highest mean levels of mercury at 0.55 ug/g (ppm), which is greater then OMOE's maximum recommended consumption limit of 0.5ppm. Both Chaucer and O'Sullivan (0.39 and 0.38 ug/g respectively) have mean mercury concentrations within the upper and lower limits OMOE's recommended consumption guidelines. Thus consumption of fish from these lakes should be limited. Walleye from both Esnagami and Briarcliff Lake had mean mercury concentrations situated at below OMOE's lower restriction limit of 0.26 ppm

Mercury levels found in Walleye from the Aroland area appear consistent with lakes from similar latitudes. Simoneau et al. 2005 found that mercury concentrations in Walleye with a standardized length of 350mm from Eastern Canada (latitudes 46°15'00'' N to 50°51'28'' N) ranged from 0.17 to 0.79ppm. Walleye from the Aroland region ranged from 0.22 to 0.55ppm for a standardized fish length of 380mm.Comparisons to this area must be examined carefully as water chemistry and land-use between the two areas vary Lavigne et al (2010) also found a significant correlation between walleye length and Hg concentrations. Similar to Aroland lakes 50% of the fish sampled in Quebec were above Health Canada's recommended threshold of 0.5ppm.

1.3.2 Comparison of Chemical Variables that Affect Hg Levels in Walleye

Results from the Kruskal-Wallis ANOVA found that statistically significant differences were present in the ranks of DOC, alkalinity, iron, pH, and sulfur. Ironically there was no statistical difference for Hg level in water and sediment between the lakes, even though there is a large variation of Hg within the fish of the same lakes.

Melchett Lake which had the highest concentrations of Hg in walleye (0.55 ug/g), also had the statistically significant highest concentration of DOC at 11.34ppm (R:40.5, p=0.000), and lowest rank of alkalinity (50.62ppm) (R: 9.6, p=0.000) for all study lakes. These results suggest that Hg levels in Walleye from Melchett Lake may be due to the lake having the highest levels of DOC, and the lowest levels of alkalinity and pH.

Although pH was not picked out as a significant predictor of mercury concentration by stepwise multiple regression within this study, studies by Greenfield et al 2001, found pH to be important. As previously mentioned pH has been shown to be an effective indicator of mercury levels within aquatic systems. However lakes within the Aroland area all had similar circum-neutral pH levels (only varying between 7.1 and 7.7), whereas lakes in Greenfield et al. 2001 varied between 5.6 and 9.1. Thus pH may be less of a factor on mercury levels in lakes in the Aroland study due to similarity between pH levels,

Furthermore although total mercury levels in water and sediment do not vary between the lakes, higher levels of DOC and lower alkalinity and pH may be increasing the microbial methylation rates within the Melchett, making it more available to enter the food chain. This appears true in this study as Esnagami Lake, which was statistically found to have the lowest Hg levels in fish (0.22 ug/g), ranked highest in pH with a mean of 7.67 (R: 42.4, p=0.000) and alkalinity concentration with a mean of 80.7ppm (R: 47.8, p=0.000), and lowest in DOC concentration (6.41ppm) (40.5, p=0.000).

1.3.3 Spatial and Biological Factors Affecting Mercury Concentrations in Fish Tissue

Mercury concentrations in fish are a result of numerous biological, chemical, environmental and spatial factors. In this particular study fish length and wetlands area present in the lakes watershed were positively correlated and inversely correlated with watershed area and % wetlands in the watershed. Results from the stepwise multiple regression suggest that chemical variables such as pH, DOC, and alkalinity did not appear to have a significant relationships to Hg accumulation in walleye, despite being documented as highly important variables in the distribution of mercury in aquatic systems. The results are both consistent and inconsistent with similar studies found in previous literature.

1.3.3.1 Length

Larger, older fish have higher levels of mercury concentrations as they have consumed more mercury for a longer a period of time compared to that of a smaller younger fish. Results from the linear regressions performed on fish length and mercury concentration data suggest the same is true for lakes within the Aroland study area. Furthermore when compared with other variables that have been linked to affecting mercury levels within aquatic systems the backward stepwise multiple regression found that length statistically explained a large portion of the Hg variability within the Aroland study area, (β=0.559, p=0.00005). Thus as fish length increases so does mercury concentration. Studies by Rose et al, (1999), and Sonesten, L., (2003), found similar results and indicate that fish size (length) is one of the most important factors affecting mercury concentrations in all species of fish.

Greenfield et al. (2001) used a regression tree analysis of spatial, biological and chemical data to predict mercury levels in yellow perch in Northern Wisconsin. Body condition (which was based on results of a linear regression between fish length and weight) of Yellow Perch was found to be a strong biological predictor of Hg levels in the biological regression tree and the combined multiple regression model. Rather than just length, Simoneau, et al (2005) found fish growth rates to be the biggest influence on Hg concentrations in 4 northern Quebec lakes. The authors concluded that difference in fish growth rates from lake to lake dominated all other environmental factors to account for differences in Hg concentrations in walleye populations. Thus lakes with populations of older, slower growing fish were found have higher mercury concentrations then that of lakes with younger, faster growing fish of the length.

Lavigne et al (2010) found similar results for Walleye and Northern Pike populations throughout the province of Quebec. The author used von Bertalanffy growth models to estimate ages of fish specimens for a given length. A quadratic regression model was used to determine Hg concentrations for standardized lengths. It was found that slower growing walleye and northern pike had much high mercury concentrations then faster growing fish.

Proper aging structures were not taken from Walleye sampled from the Aroland study area, higher Hg levels in fish from Melchett Lake may be due to slower growth rates. Likewise lower Hg levels in Esnagami and Briarcliff lakes could be accounted for by faster growth rates.

Although study lakes are in a relatively close geographic proximity, significant variation in fish growth rates between lakes seems unlikely, Simoneau et al 2005, found that it does occur, not only from lake to lake, but also within lakes. Therefore a study looking at growth rates and mercury levels within the Aroland region maybe a very viable research opportunity to better explain the variation.

1.3.3.2 Wetland Area

Results from the stepwise multiple regression (Table 5) suggest that wetland abundance contributed most of the variation of fish Hg levels between lakes, as it had the highest beta coefficient (β= 6.44). As wetland abundance increases within a watershed, so does Hg levels in fish. This is consistent to results found in similar studies.

Castro et al. (2007) found significantly higher levels of Hg in brook trout from Maryland streams that had higher abundance of wetlands within its catchment area compared to that of streams with no wetland areas. Rudd, (1995) also found similar results, in which stained colour lakes that received large amount of inflow from wetlands had much higher levels of MeHg.

Referring to Table 1.1 of the results, Melchett Lake has a wetland area of 8.53 km^2, which is second lowest of all the study lakes, yet Walleye from the lake had statistically higher levels of Hg. Furthermore the Krustal-Wallis ANOVA illustrated that DOC was ranked highest in Melchett Lake. This suggests that Melchett Lake may be receiving DOC and Hg from sources other then Wetlands. The area itself is very remote and thus direct inputs from anthropogenic sources are highly unlikely. However the area is situated in the heart of the boreal forest, which is prone to both natural (forest fires) and anthropogenic disturbances (logging). Both of which maybe be present and contributing to DOC and Hg levels within the Melchett Lake watershed. There are a number of noteworthy papers that support this theory. Garcia and Carignan (2000), found that extensive logging significantly increased the amount of Hg, in Northern Pike in Boreal Shield Lakes, compared to reference lakes with no disturbance. In a similar study Garcia and Carignan, (2005) used stable isotopes of nitrogen to determine trophic position of the fish. As suspected Hg increased with trophic status, however mercury availability was significantly higher at the base of the food chain in disturbed watersheds. Furthermore Hg concentrations in fish were significantly related to the disturbance size: lake size ratio. This ratio was highly correlated with DOC levels within the study lakes.

1.3.3.3 Watershed Area and % Wetlands in Watershed

Results from the stepwise multiple regression found that both watershed area and % wetlands in watersheds to be significant negative predictors of Hg concentrations in fish ($\beta = -5.797$, $p=0.0000$ and $\beta = -1.52$, $p=0.0000$). These results suggest that mercury concentrations increase as catchment size becomes smaller, and wetlands become less abundant. Both results appear inconsistent and contradictory to what is been found in similar studies, and also data from this study. As mentioned the general consensus from prior studies suggest that mercury levels increase with increasing watershed size and wetland abundance. These results also contradict other predictors from the same multiple regression, as wetland area (km^2) was found to be a strong positive predictor for Hg levels. Possible explanations for this are that lakes chosen for this study had large watershed areas in comparison to lake area. This would then increase the watershed area: wetland abundance ratio, thereby reducing the % of wetland. The numbers used in watershed area are finite and are real approximations of the amount of wetland within each watershed. Data from this study as well as previous studies suggest that wetland area (km ^{2}) rather then wetland % is a better predictor of Hg levels within the study.

Another explanation for these contradictions of data is the lack of measurement of the hypolimnion area within the lake area model. As methylmercury is formed in anoxic conditions, lakes with a larger area of hypolimnion will produce more methylmercury, compared to that of shallow unstratified lakes. Results from Nilsson and Hakanson, 1992, agree with this as they found that high mercury concentrations were correlated with lake colour in deep stratified lakes with large hypolimnions. Thus it is possible that lakes in the Aroland study area all receive Hg from surrounding wetlands, however lakes with a large area of hypolimnion are able to methylate higher concentrations of mercury, making it more available and visible within the fish tissue.

1.4 Conclusions and Future Work

It is difficult to pinpoint the factors influencing mercury concentrations in Walleye from the Aroland study area. It may result from a combination and interaction between a few particular biological, chemical, and spatial factors. Specifically fish length, wetland abundance (km^2) were picked out by a stepwise multiple regression as the best predictors of Hg levels in fish. This is consistent with previous literature and likely both these factors are contribute to Hg levels in lakes and aquatic biota from the Aroland region. The multiple regression also suggests watershed area and % wetland abundance as negative correlated predictors of Hg levels. However this contradicts data from both this project, and previous literature, making it difficult to make informed conclusions.

Although no chemical variables were chosen as good predictors in the stepwise multiple regression, results from a between lake comparison of lake water data using a

Kruskall-Wallis ANOVA, suggest that not all chemical variables should be overlooked. Melchett Lake which had the highest levels of Hg in Walleye, ranked highest in DOC, and lowest in alkalinity, and pH (second lowest ranked), all of which are consistent with higher levels of Hg. In contrast Esnagami Lake, which had the lowest levels of Hg in Walleye, was found to rank lowest, in DOC, and iron, and highest in alkalinity and pH. This suggests that chemical factors do a role Hg levels in the aquatic environment.

Other factors that weren't included in this study may also be contributing to Hg concentrations. Growth rates of the fish, amount of disturbance (both natural and anthropogenic), and lake depth (hypolimnion area) were not covered in this project, due to logistical constraints, however all have shown the potential to induce changes in Hg levels in previous studies. In future studies similar to this, these variables be assessed to allow to enhance understanding of the exact variables influencing mercury within the aquatic system.

2. The Influence of Geology on Lake Quality/Characteristics Near Aroland Ontario

2.0 Introduction

The chemistry of natural surface water is influenced by a variety of external sources. Interactions with the atmosphere, watershed characteristics and land use all play important roles on the chemical characteristics of the lake. However one of the most important influences on the chemical characteristics of surface water is the erosion and weathering of surrounding rocks and minerals within the lakes watershed (Hem, 1985).

Erosion and chemical weathering is an important process in the hydrogeochemical cycle of the elements. In this process water acts as both a reactant and a transport agent for dissolved solutes and particulates from the land to surface water (Stumm and Morgan, 1996).

Many factors control the rate of weathering and the dispersion of metals and other elements from rock into the aquatic environment. Temperature, pH, redox potential and time in which water is on contact with rock, all affect the solubility of each metal and their capability to be transported throughout a watershed (Chen and Brantley, 1997; Chuan et al; 1996).

During chemical weathering, rocks and minerals are dissolved into solutes. These are then transported through the watershed to be deposited into surface water (or groundwater)(Hem, 1985; Lavergren, 2005). The chemical composition of ground waters and surface waters often reflect the chemical characteristics of the rock, soil, and sediment that exist within a watershed (McCartan et al, 1998).

Precipitation travels through an aquatic system as surface runoff, shallow interflow, groundwater flow through unconsolidated surficial materials, or bedrock fractures (Newton et al, 1987). Generally surface water and shallow interflow water moves quickly through the watershed. This leaves little time for water to react with minerals in the soil. Groundwater, which moves much more slowly through the watershed, has time to react with geologic materials. Given sufficient time, groundwater can react with low solubility minerals (Newton et al, 1987).

A lake's water chemistry commonly reflects the geochemistry of the underlying geology (Gibson et al. 1995). A considerable amount of literature exists pertaining to the influence of geology on water chemistry. Very often geology plays an integral part in lake health. One of the most well known examples of this is the presence of carbonate minerals such as calcite and dolomite ($CaCO_3$ and $CaMg(CO_3)$). Carbonate minerals are widely distributed and readily dissolve in water (Stumm and Morgan, 1996). Along with carbon dioxide (CO_2) and bicarbonate (HCO_3^-), carbonate plays a major role in the pH buffering system of natural waters. This phenomena is known as alkalinity or acid neutralizing capacity (ANC), and is an important mechanism to withstand abrupt changes in pH (Wetzel, 2001). Lakes found within geologic units containing carbonates will often have significantly higher levels of alkalinity, as well the cations of calcium and magnesium (Gibson et al, 2005)

Surface water found in areas of granitic and quartzite bedrocks, similar to that of lakes in the Canadian Shield, typically have lower ANC due the lack of carbonates in surrounding rock. Lakes in these areas are more prone to a decrease in pH, due to the addition of acidic material (i.e. acid rain d). The inability to buffer changes in pH can have devastating consequences on aquatic organisms (Bouchard, 1995;Giovanoli et al, 1988).

The chemical weathering of sulphide bearing rock can also effect pH. When oxidation in the presence of water occurs, sulphuric acid is generated (H_2SO_4). The chemical weathering reaction of pyrite (FeS_2), which is a common sulphide mineral is described as the following:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$$

The sulphuric acid produced then degrades other minerals such as silicates, which in turn release metals and other elements into the aquatic environment (Lavergren, 1995). Such reactions can dramatically increase levels of sulphate, major cations, and other metals in a lake system.

Mercury is found naturally in varying concentrations throughout most igneous and sedimentary rocks (Hem, 1995). However, numerous studies have shown that sulphide mineralization in rock is often associated with elevated levels of metals including mercury. In particular black shales have a high occurrence of metals and trace elements. Black shale is a sedimentary rock that may be deposited in stagnant aquatic conditions with large amounts of organic and inorganic material. Decomposition of the organic material creates anaerobic conditions, which completely reduces all sulphur into sulphide, and causes metals to complex with sulphide ions creating suphide minerals in the sediment (Lavergren, 2005;Rasmussen et al 1998;Loukola-Ruskeeniemi et al;2003),

Black shale deposited in such conditions have exhibited high levels of copper, sulphur, nickel, carbon, zinc, cadmium, and mercury. Mercury anomalies were found after studies performed in the Thunder Bay, area show that stream sediments underlain by Rove black shale has significantly higher levels of trace metals, Hg, Zn, As, Cd, than that of the background area which was underlain by Archean metavocanics. Mercury and trace metal anomalies in this area are attributed to weathering and deposition of the parent Proterozoic Rove and Gunflint formations. Sulphide mineralization in black from the Proterozoic are generally found be higher in mercury concentration then that of the Archean and Phanerozoic ages (Rasmussen, et al, 1998).

Igneous rocks have also been associated with mercury anomalies. Research from Kaminak Lake, near Hudson Bay, illustrated that Hg concentrations were much higher in fish and water in areas of the lake that were underlain by sulphide rich metavolcanics. Anomalies within the lake water were attributed to weathering of mercury rich sulphides, as significantly large variations occurred not only within lakes in the same region but also within Lake Kaminak (Shilts and Coker, 1995). Mercury concentrations were so high in Kaminak that a commercial fishery was forced to move to nearby Kaminuriak Lake (which was not underlain by sulphides), as the Hg levels in Lake Trout exceeded the national consumption guidelines of 0.5ppm (Shilts and Coker, 1995).

The purpose of this paper is to examine and quantify the similarities of water chemistry of the Aroland study lakes in relationship to geochemistry of surrounding geology within each lakes watershed. Study lakes will be compared to each other based on the chemical characteristics of their water, and sediment. Furthermore, the chemical characteristics of each lake will be compared to the geochemistry of their watersheds, using a variety of water/rock interaction experiments, and X-ray diffraction analysis. The chemical characteristics of each lake should closely resemble the geochemistry of the watershed and shoreline, indicating a geological influence. Furthermore mercury levels in both lake water and sediment, as well in the water/rock interaction experiments should be higher in lakes where mercury content is naturally higher in surrounding rock. These high mercury concentrations in rock units and to a further extent receiving lake water and sediment will be highly associated with the presence of sulphide mineralization.

2.1 Methods

2.1.1 Field Sampling: Water and Rock

The same procedures discussed in chapter 1 were used for this portion of the study for the collection of lake water. Rock samples were collected from outcrops surrounding each of the study lakes. A geological map of the area (Map 2102 Tashota-Geradlton Sheet, Geological Compilation Series; 1:253440) was used to ensure that all of the lithologies or rock types surrounding each lake were sampled. Large quantities of rock were broken off throughout each lithology and bagged in large heavy-duty plastic bags. Rock specimens were brought back to Lakehead University's Department of Geology where they were crushed and mechanically separated and bagged by grainsize. Rock were then were crushed by hand using an agate mortar and pestle. A mechanical agate grinder was then used to further grind the particles to the appropriate size of 1-30μm for X-ray diffraction analysis.

2.1.2 Laboratory Procedures for Chemical Analysis of Water

Laboratory procedures for water analysis were discussed in Chapter 1. Analysis was conducted for alkalinity, DOC, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Ma, Mg, Na, Ni, Pb, S, Sr, Ti, V, Zn, pH, and total Hg in lake water and Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn, and total Hg in lake sediment. The same procedures were used in this portion of the study.

2.1.3 Statistical Analysis of Water Chemistry

Statistical analysis of water and sediment data followed the same process two step process:

i) **Kruskal-Wallis ANOVA**

A Kruskal-Wallis ANOVA was run using the statistical software package STATISTCA 7.0 to determine if significant differences of chemical concentrations in water existed. As mentioned in Chapter 1 the Kruskal-Wallis ANOVA is a nonparametric alternative to the ANOVA. Significant differences between lakes was assumed for ranks of chemical concentrations when $p < 0.05$.

ii) **Stepwise Discriminant Function Analysis (DFA)**

STATISTICA 7.0 was used run a forward stepwise DFA on lake water and sediment data. Computationally DFA is similar to the ANOVA/MANOVA test, however DFA has the ability to determine what chemical variables contribute to the discrimination between lakes (Hill and Lewicki 2006). In a DFA variables are discriminated by considering the ratio of negative terms to the positive terms. In addition variables that are highly correlated are eliminated from the final analysis

Prior to analysis, variables that had all samples below the instruments detection limit were removed. In the case of variables that only had a few samples below detection limit, the method discussed by Geib and Einax (2001), in which numbers representing 1/2 the instruments detection limit are inserted and used in the analysis. Because the test assumes that the data follow a normal distribution, water and sediment data was log transformed to provide a more normal distribution.

The stepwise DFA analysis used Wilks λ as the separating statistic and the F statistic to enter/remove variables. A graphing function in STATISCA was then used to produce a scatterplot of function 1 vs function 2. Standardized coefficients were used to interpret each function. It is assumed that higher the coefficient of a variable the greater the contribution to the discrimination of the lakes.

2.1.4 X-Ray Diffraction

Samples were analyzed using a Panalytical Expert Pro Diffractometer at the Lakehead University Instrumentation Laboratory. Start and end positions [°2Th.] of the detector were 6.0 and 76 respectively, using a 0.0260 step size and a copper anode.

X-Pert Highscore Plus software was used to analyze and compare peaks in the XRD data to the ICDD mineral databases and determine which minerals were present in each rock samples

2.1.5 Water/Rock Interaction Column Experiment

The purpose of the column experiments was to quantify chemical constituents in water by modelling chemical weathering of geologic units found within each lakes watershed, and water /rock interactions. Methods for the experiment closely resembled that of an experiment performed by Godwin (2010)

Six clear PVC piping with an inner diameter of 10.2cm were used to emulate lake water and rock interactions/weathering. Each column was equipped with black end caps, with the bottom end cap having a hole to allow for insertion of a syringe lure and valve for water sampling.

Geological maps were used to measure the surface area of each lithology in contact with the shoreline from each lake. A ratio was calculated based on the amount of each rock type was in contact with each lake. Rock samples were then measured out and weighed accordingly in respect to the calculated ratios.

Crushed rock with grainsize between 0.5mm and 1.0mm from each lake were placed in 100μm nitex cloth (in the calculated ratios) that had been sewn into sleeves. Sleeves were then hung separately in the each column and 4L of DDW. DDW was chosen to represent lake water as it allows to easily depict the chemical reactions and chemical leaching that is occurring between the rock and the water. A sixth column was used a blank, and thus had only an empty nitex sleeve and DDW within it.

Columns were sampled at 1,2,7,14, and 30 days and analyzed at LUEL for metals, and mercury. The same laboratory procedures for the analysis of lake water mentioned in chapter 1 were followed.

2.2 Results

2.2.1 Lake Water Analysis and Statistical Results

Mean concentrations were found for all water chemistry parameters. These results were illustrated in Chapter 1 (Table 1.3).

A Kruskal-Wallis ANOVA was performed on water samples taken from each lake to evaluate if significant differences among ranks of water chemistry parameters existed between lakes. Table 2.0 shows the results from the test. The Kruskall-Wallis ANOVA illustrates that there is a significant differences in water chemistry among the study lakes for the majority of the parameters. All parameters except aluminum and barium were shown to have significant differences in ranks between lakes.

Table 2.0. Table showing Results from the Kruskal-Wallis ANOVA comparison of ranks between water chemistry parameters, where H= the kruskal wallis statisic (approximation of the Chi-squared distribution)(R= ordinal rank median rank of concentrations, and p=significnance <0.05

Parameter and Test Significance	**Melchett**	**Esnagami**	**Briarcliff**	**Chaucer**	**O'Sullivan**
DOC-H_4= 27.19, p=0.000	R=39.750	R=5.650	R=32.700	R=27.250	R=30.820
Al-H_4=4.70, p=0.3194	R=28.550	R=25.700	R=21.250	R=24.950	R= 34.321
Alk- $H=_4$ 46.725, p=0.000	R=9.450	R=46.800	R=11.550	R=25.500	R=39.428
Ba- $H=_4$ 5.329, p=0.255	R=20.400	R=30.050	R=27.850	R=29.900	R=28.786
Ca- H_4=45.73 p=0.000	R=8.700	R=43.900	R=12.300	R=25.500	R=41.300
Fe- H_4= 11.376, p=0.023	R=29.800	R=13.400	R=35.350	R=31.450	R=27.500
Mg- H_4= 16.216, p=0.003	R=34.750	R=12.450	R=34.900	R=21.400	R=32.143
Ma- H_4= 46.378, p=0.000	R=8.500	R=45.70	R=12.500	R=25.500	R=46.214
pH- H_4= 35.617, p=0.000	R=20.000	R=41.400	R=5.500	R=39.200	R=30.286
K- H_4= 22.783, p=0.000	R=36.300	R=22.150	R=44.100	R=16.750	R=20.857
Na- H_3= 47.145, p=0.000	R=6.100	R=40.200	R=14.900	R= 25.700	R=44.000
Sr-H_4= 47.890, p=0.000	R=7.300	R=38.000	R=13.700	R=26.430	R=45.036
S-H_4= 46.076, p=0.000	R=24.550	R=42.000	R=15.200	R=6.750	R=42.857
Hg-H_4=4.28, p=0.3692	R=21.000	R=42.400	R=7.250	R=16.500	R=15.375

Discriminant Function Analysis

A forward stepwise discriminant analysis was used to determine if significant differences in water chemistry among study lakes occurred. A DFA is a parametric test with the same assumptions as ANOVA or ANCOVA (mentioned in chapter1). Green, 1971 demonstrated that even with non-parametric data, DFA still provides statistically sound results for environmental data. In a DFA variables are discriminated by considering the ratio of negative terms to the positive terms. In addition variables that are highly correlated are eliminated from the final analysis. For instance alkalinity was correlated with calcium and manganese, while potassium was negatively correlated with aluminum. This most likely resulted in Ca, Ma, and Al being eliminated from the final discriminant analysis. Results of the DFA are iillustrated in Figure 2.0 with a scatterplot of discriminant function 1 vs. discriminant function 2. DFA test results found that 95% of the variance was accounted for in 2 functions. Function 1 accounted for most of the variability between lakes with an eigenvalue of 208.01 and 87.6% of the variability.

Standardized coefficients suggest root 1 is explained by alkalinity (1.44) and potassium (-1.41). Function 2 had an eigenvalue of 17.42 and together with function 1 accounted for 7.4% of the proportion of variability. Standardized coefficients suggest that root 2 is explained by sulphur (2.07), and potassium (-1.34).

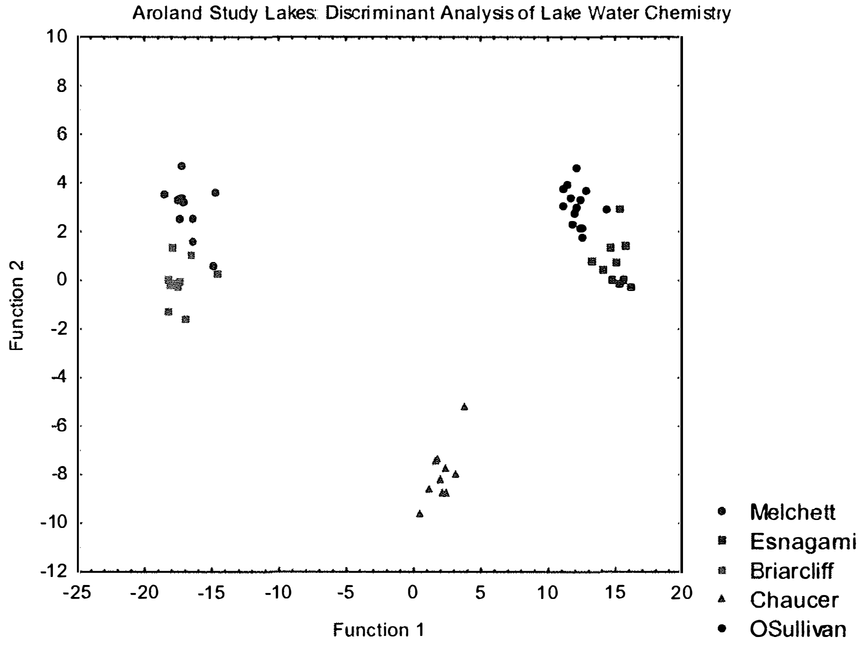

Figure 2.0. Scatterplot illustrating results from DFA of Lake Water Chemistry. .The test had 11 steps, with the Wilksλ = 0.00001. and p<0.0000

Figure 2.0 illustrates that Melchett and Briarliff Lakes are similar but distinct from Esnagami and O'Sullivan Lakes, which are also closely grouped as well as Chaucer Lake, which is distinct from all lakes. As mentioned standardized coefficients suggest that function 1 is defined by alkalinity (1.44) and potassium, suggesting that Melchett and Braircliff lake are defined by low alkalinity and high potassium concentrations, whereas Esnagami and O'Sulivan Lakes are defined by high alkalinity and low potassium concentrations. Chaucer Lake appears to cluster around the"0" mark of function 1, which indicates it has neither high or low levels of alkalinity and potassium when compared to the other lakes.

Standardized coefficients suggest that function 2 is defined by sulphur (2.07) and potassium (-1.34). Referring to Figure 2, Melchett and O'Sullivan Lake are defined by high sulphur and low potassium concentrations, whereas Chaucer is isolated with low sulphur and high potassium concentrations. Both Esnagami and Briarcliff are relatively neutral on the axis.

Function 1 and function 2 appear to contradict each other in regards to the discrimination of potassium between each lake. Because function 1 accounts for significantly more variation then function 2, it is assumed that function 1 is more reliable. Thus low alkalinity levels, as well as high potassium and sulphur concentrations characterize Melchett Lake. Chaucer is discriminated by low sulphur, while Briarcliff is defined by low alkalinity and high potassium. Furthermore Esnagami is characterized by high alkalinity and low potassium concentrations with regards to the other study lakes.

2.2.2 Geological Data Results

2.2.2.1 X-Ray Diffraction

X-Ray diffraction is a common method used by geologists and minerologists to examine the chemical make up of unknown solid materials. X-Ray diffraction was used to analyze the chemical composition of rocks surrounding lakes in the Aroland study area. Tables 2.2– 2.6 show the results from the X-Ray diffraction analysis.

Briarcliff

Rock samples were taken from 3 different locations from around Briarcliff Lake. X-ray diffraction analysis illustrates that all areas had a very similar geochemical make up consisting of predominantly SiO_2 (quartz) and $NaAlSi_3O_8$ (albite). Other minerals containing common elements such as potassium, iron, calcium and aluminum were also found to be present within the samples, in minerals such as fluorannite, microcline, and clinochlore. Major minerals found within rock samples from Briarcliff Lake and their general abundances are summarized in Table 2.2.

Chaucer Lake

Rock samples were taken from 4 locations surrounding Chaucer Lake. Similar to Briarcliff, both quartz and albite were commonly found in each sample. Results also illustrate that rock surrounding Chaucer Lake has minerals such as microcline, and flourannite containing a variety of common metals (Al, ,K,Fe, and Mg). Table 2.3 summarizes results from XRD analysis for Chaucer Lake.

Table 2.1. X-Ray Diffraction Results for Briarcliff Lake. Mineral abundances: Dominant-x, Moderate-o, Trace-*, and Absent-a

Sample	Quartz	Albite	Fluorannite	Microcline	Dickite	Clinochlore
1	x	o	o	a	a	a
2	x	o	a	o	a	a
3	x	o	a	a	*	o

Table 2.2. X-Ray Diffraction Results for Chaucer Lake. Mineral abundances: Dominant-x, Moderate-o, Trace-*, and Absent-a

Sample	Quartz	Albite	Microcline	Clinochlore	Phlogopite	Flourannite
1	x	o	o	a	a	o
2	x	o	a	a	o	a
3	x	x	a	o	a	a
4	x	o	a	a	o	a

Melchett Lake

Rock samples were taken from 4 different sites surrounding Melchett Lake. Results from the X-ray diffraction analysis show that both quartz and albite were found in all samples. Similar to both Briarcliff and Chaucer, the minerals microcline and fluorannite were also found to be present in samples from Melchett Lake. Again such minerals contain common metal elements such as Al, Fe, and Mg. Table 2.4 summarizes major minerals found in rock samples from Melchett Lake.

Table 2.3 X-Ray Diffraction Results for Melchett Lake. Mineral abundances: Dominant-x, Moderate-o, Trace-*, and Absent-a

Sample	Quartz	Albite	Phlogopite	Microcline	Flourannite
1	x	o	a	a	a
2	x	o	*	a	a
3	x	o	a	*	*
4	x	o	a	a	a

O'Sullivan Lake

Rock samples were taken from 4 locations surrounding O'Sullivan Lake. Although quartz and albite were found to be present in all samples, other minerals that were not present in samples from other lakes. Minerals such as Ankerite, Carlinite, and Koninckite appear to be present in samples from O'Sullivan Lake, all of which were not found in any other samples. The chemical composition of these minerals is a combination of common metals such Fe, Mg, Mn, Al.. Major minerals present within rock from O'Sullvan Lake is summarized in Table 2.5

Esangami Lake

In total rock samples were taken from 3 locations surrounding Esnagami Lake. Similar to rock from other study lakes, quartz and albite are found to be quite common in rocks surrounding Esnagami Lake. Unlike samples from the other study lakes, sample #1 from Esnagami appears to have the mineral dolomite present.

Other minerals found again are fairly similar with the other lakes geology, with Clinochlore and Fluorannite, being present. Table 2.6 illustrates results from XRD analysis of rocks from Esnagami Lake.

Table 2.4. X-Ray Diffraction Results for O'Sullivan Lake. Mineral abundances: Dominant-x, Moderate-o, Trace-*, and Absent-a

Sample	Quartz	Albite	Chinochore
1	x	o	x
2	x	o	x
3	x	o	x
4	x	*	x

Table 2.5. X-Ray Diffraction Results from Esnagami Lake. Mineral abundances: Dominant-x, Moderate-o, Trace-*, and Absent-a

Sample	Quartz	Albite	Chlinochlore	Dolomite	Fluorannite
1	x	o	o	x	o
2	x	o	a	a	o
3	x	o	x	a	a

2.2.2.2 Column Experiments

Water/rock interaction column experiments were ran for 30 days in the spring of 2010. Water from the experiments were sampled on days 1, 2, 7, 14, and 30, and analyzed for metal cations. Table 2.8 shows initial results from Day 1 and final results from day 30 and the % change in concentration between days 1 and 30.

Table 2.8 illustrates that most chemical parameters from each column (lake) generally increased throughout out the entire experiment, with the exception being Chaucer Lake , in which 8 of the 14 detectable parameters decreased. In each column the levels of As, Be, Cd, Co, Cr, Mo, Pb, Ti, and V remained below detection limit for the entire experiment.

Table 2.6. Table displaying results from Day 1 and Day 30 sampling and % change from column experiment . Heading uses shortforms for lake names: Briarcliff=Briar, Chacer: Chauc, Esnagami: Esna, Melchett=Melch, O'Sullivan=O'Sul. It assumed all columns started at concentrations of 0, as DDW was used as reagent

	Briar Day1	Briar Day30	% Change	Chauc Day 1	Chauc Day 30	% Change	Esna Day1	Esna Day30	% Change	Melch Day1	Melch Day30	% Change	O'Sul Day1	O'Sul Day30	% Change
Aluminum	0.025	0.133	432	0.133	0.028	-375	0.089	0.053	-67.9	0.036	0.023	56.5	0.058	0.131	125.8
Arsenic	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Barium	0.008	0.022	175	0.02	0.015	-33.3	<DL	0.008	n/a	0.003	0.024	700	<DL	0.013	n/a
Berryllium	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Calcium	6.289	23.747	277	6.469	6.405	-1.0	1.197	8.311	594	2.003	10.183	408.4	5.517	27.487	398.1
Cadmium	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	0.001	n/a	<DL	<DL	n/a
Cobalt	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Chronium	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Copper	0.032	0.009	-255	0.049	0.008	-512.5	0.008	0.005	-60	0.05	0.031	-61.3	0.019	0.01	-90
Iron	0.239	0.2	-19.5	0.412	0.092	-347.8	0.056	0.879	147.7	0.05	0.021	-138.1	0.067	0.128	91
Potassium	0.95	1.43	50.5	1.71	1.81	5.85	0.69	2.66	285.5	0.82	1.57	91.5	0.36	0.62	72.2
Magnesium	1.11	2.52	127	1.13	1.08	-4.63	0.31	1.9	512.9	0.33	1.07	224.2	0.48	2.3	182
Manganese	0.0749	0.0146	-413	0.2856	0.5448	90.7	0.006	0.2938	479.9	0.0395	0.8838	2137.5	0.0089	0.0346	288.8
Molybdenum	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Sodium	0.61	0.59	-3.4	0.7	0.51	-37.3	0.49	0.85	73.5	0.46	0.57	23.9	0.56	0.71	37.5
Nickel	0.003	<DL	n/a	0.021	0.014	-50	<DL	<DL	n/a	0.002	0.002	0	<DL	<DL	n/a
Lead	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Sulfur	1.7	1.61	-5.6	4.36	2.88	-51.4	0.54	0.62	14.8	1.46	2.08	42.5	0.8	0.76	-5.26
Strontium	0.007	0.023	229	0.008	0.009	12.5	<DL	0.013	n/a	<DL	0.014	n/a	<DL	0.02	n/a
Titaniuim	<DL	0.014	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Vanadium	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a	<DL	<DL	n/a
Zinc	0.023	0.003	-660	0.029	0.008	-162.5	0.003	0.002	-50	0.01	0.004	-150	0.013	0.002	-550
Hg (ng/L)	22.4	76.46	241	25.78	31.83	23.5	4.51	28.89	540.6	8.68	46.81	439.3	9.12	62.45	586

Because DDW was used as the reagent all parameters began the experiment at 0ppm. In terms of parts per million increases, Ca displayed the most dramatic increases in concentration in all lakes except Chaucer, which showed a decrease between day 1 and day 30. O'Sullivan and Briarcliff were found to have the highest finals Ca concentrations with 27.5 mg/L and 23.7mg/L respectively, while Chaucer had the lowest at 6.4mg/L. Figure 2.1 illustrates the changes in calcium concentration in column over the entire study period. In terms of ppm changes increases, potassium, magnesium and sulphur also displayed fairly moderate increases in concentration (except for Chaucer) between days 1 and 30 of the experiment. Figures 2.2 to 2.6 show the changes in K, Mg, and S concentrations respectively within column water over the entire study period. The graphs show that highest K levels were found in columns from Esnagami (2.66mg/L) and Chaucer Lakes (1.81mg/L), with the lowest concentration being found in the O'Sullivan column (0.62 mg/L). Furthermore the graphs demonstrate the highest levels of Mg were found in columns from Briarcliff (2.52mg/L) and O'Sullivan (2.30mg/L) while the lowest was found in Melchett Lake (1.07mg/L). Finally Figure 2.6 illustrates that the highest levels of sulphur were found in Chaucer and Melchett lakes with concentrations of 2.88 and 2.08mg/L respectively. The lowest sulphur levels were displayed in O'Sullivan with a final concentration of 0.76 mg/L.

All columns displayed significant increases in concentrations of Hg (Fig.2.5) The highest concentrations were found in columns from Briarcliff, O'Sullivan and Melchett Lakes with 76.46, 62.45 and 46.81 ng/L respectively. The lowest concentration of Hg from the final day of the experiment was found in the column from Esnagami with a concentration of 28.89ng/L. Hg concentrations in all columns appear to be steadily increasing towards the end of the experiment. Figure 2.5 illustrates changes in Hg concentration over time for each column. The rest of the graphs depicting changes in concentration in the remaining variables from the column experiments can be seen in Appendix 1.

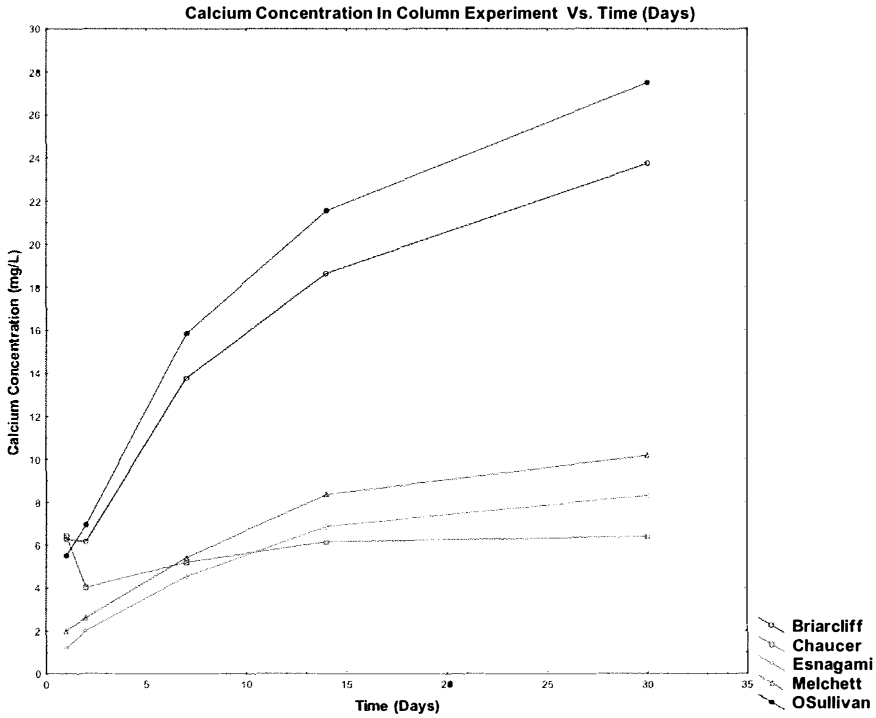

Figure 2.1. Changes in calcium concentrations in columns over time

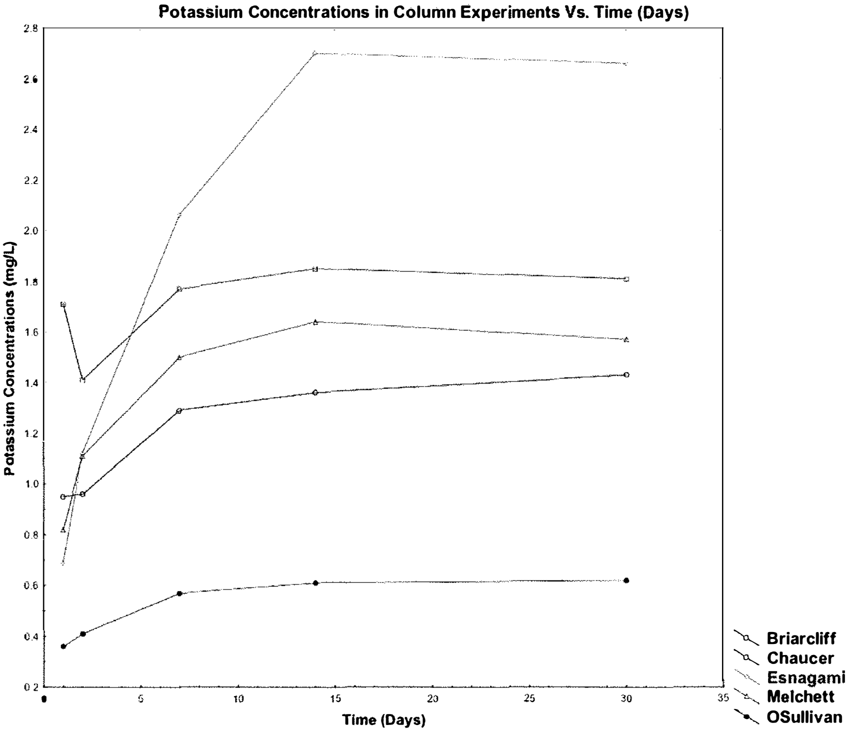

Figure 2.2. Changes in Potassium concentrations in columns over time

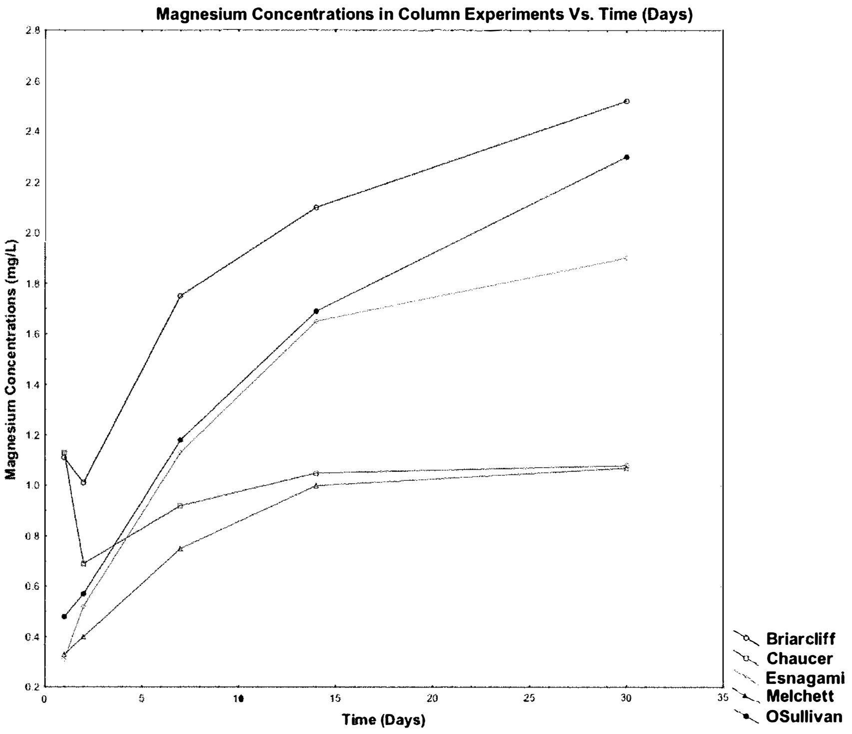

Figure 2.3. Changes in Magnessium concentrations in columns over time

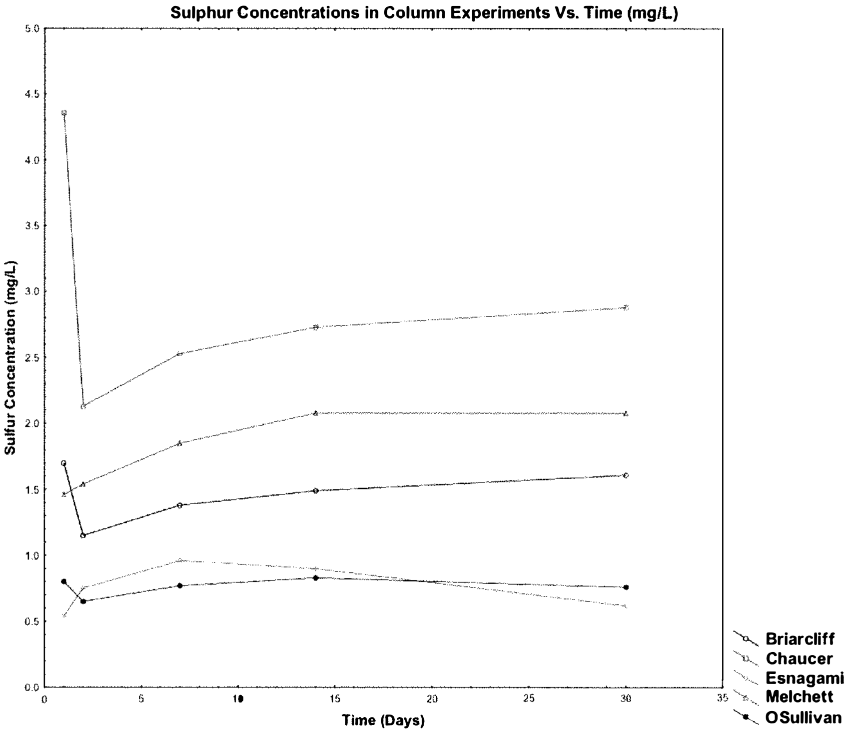

Figure 2.4 Changes in Sulphur concentrations columns over time

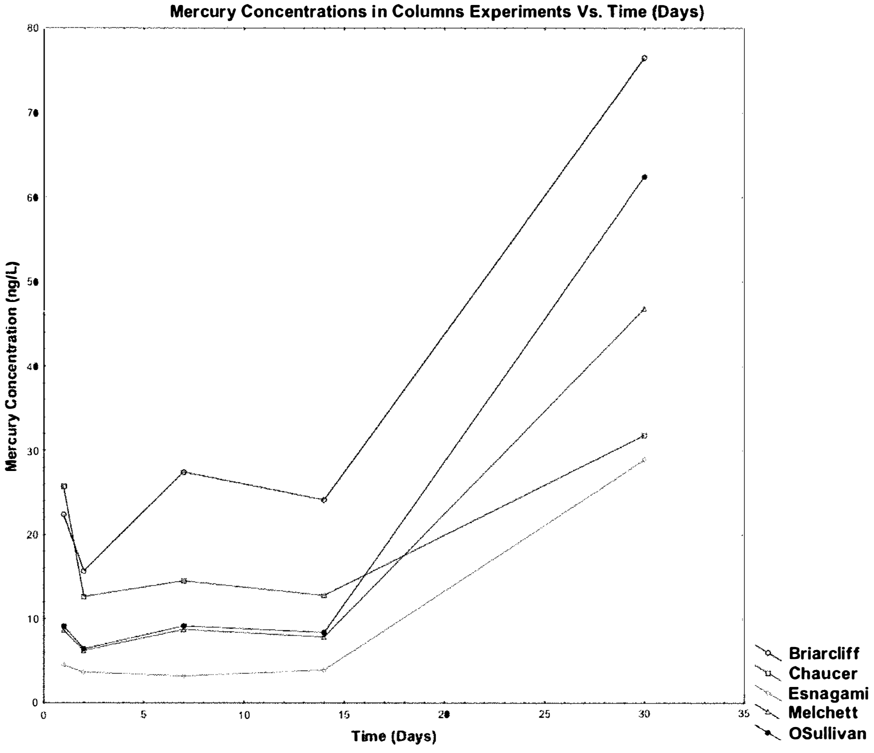

Figure 2.5. Changes in Mercury concentrations in columns over time

2.3 Discussion

Water chemistry from 5 lakes in the Aroland study area should closely resemble the geochemistry of the geology in the surrounding watersheds. The presence of sulphide mineralization within surrounding lithologies should correspond to higher mercury levels in lake water.

With the use of discriminant function analysis and nonparametric ANOVA statistics study lakes were separated based on their water chemistries. These were then compared to geochemical data from each watershed found through X-Ray diffraction and analysis and water rock interaction experiments.

Apparently surrounding geology plays a role in each lakes water chemistry. Each lake will be discussed individually.

2.3.1 Melchett Lake

DFA of log transformed water chemistry data suggest that Melchett Lake is discriminated by low alkalinity and high alkalinity and sulphur levels in comparison to other the lakes. Lake alkalinity is defined by the amount of carbonate and bicarbonate in a lake system. When present the dissolution of carbonate and bicarbonate bearing minerals greatly increase the receiving lakes ability to withstand a change in pH. XRD analysis of rock samples taken with the Melchett Lake watershed indicated that no carbonate minerals were present. These results reflect the water chemistry found in Melchett Lake as the Kruskal-Wallis ANOVA ranked the lowest lake in regards to alkalinity levels compared to the other lakes. Thus typical of most granitic seepage lakes, Melchett would have relatively low acid neutralizing capability compared that of lakes in a karst topography.

Concentrations of cations of magnesium and calcium are also commonly correlated with alkalinity as they are often associated with carbonate minerals. Results from the Kruskal-Wallis ANOVA indicate that calcium levels in Melchett Lake water rank significantly lower then other lakes, whereas Mg levels rank amongst the highest. Examination of XRD data illustrates that a number of minerals present within the Melchett Lake watershed contain Ca and Mg which may contribute to concentrations found in lake water. For example a number of the Albite minerals found within rocks from Melchett Lake were found to contain Ca, whereas the Mg bearing mineral Phlogopite was also present.

Referring to the column data experiment calcium levels were found to be some of the lowest compared to the other lakes, whereas magnesium was somewhat moderate. A reason that calcium maybe found in much lower concentrations compared to the other lakes is that most of calcium found is contained in Albite. Feldspar minerals such as Albite are a group of silicates that are fairly resistant to chemical weathering from water, especially the potassium felspars (Hem, 1989). Albite is the only source of calcium found in rock material, dissolution rates may be minimal, as exhibited by both lake chemistry and column experiment data.

Discriminant function analysis isolated Melchett Lake from other lakes by high sulphur levels. These results are consistent with column experiment data where Melchett Lake finished with a sulphur concentration of 2.08mg/L, which was second only to Chaucer Lake.

The majority of sulfur in a lake system comes from the weathering of sulphide bearing rock, which is then oxidized into sulphate in oxic lake conditions (Hem, 1989). Results from the XRD analysis found no sulphur was present in any of the minerals found in rock samples from Melchett Lake. Two possible explanations for this is the presence of elemental sulphur (not associated with mineralization) within the rocks, and/or the presence of organic sulphur compounds produced by bacteria. Hem 1989 stated that native elemental sulphur is fairly common in igneous rocks, with average concentrations found to approximately 410ppm. Thus weathering and dissolution of rock containing uncomplexed native sulphur would contribute to concentrations found within lake water.

Richards et al. (1991) found that complexed organic sulphur compounds can also contribute to sulphur levels within a lake. Studies indicated that organic sulphur compounds were bacterial dependent and have capability of adding fairly significant amounts of S to a lake system. However because bacteria produce organic sulphur compounds, optimal conditions are needed. Bacterial productions of organic sulphur have been linked to lake depth and wetland/littoral area.

DFA of lake water chemistry also suggests that potassium is a key function for discriminating among lakes. Discriminant function 1 suggests that Melchett Lake is defined by high potassium levels. Results from the Kruskal- Wallis ANOVA support this as Melchett Lake ranks among the highest in terms of K concentrations between lakes. Furthermore results from the water/rock interaction column experiments illustrate moderate amount of potassium being leached out the rock. Examination of the mineral composition from X-ray diffraction results illustrate an abundance of potassium bearing minerals, such Phlogopite (mica), Fluorranite (mica), and Microcline (feldspar). Thus as rock has been found to be a large source to aquatic systems it is evident that the chemical dissolution of potassium out of these minerals from rocks within the watershed are contributing to potassium levels within the lake water.

2.3.2 Briarcliff Lake

Discriminant function analysis of lake water chemistry illustrated that Briarcliff Lake is discriminated by the same variables as Melchett Lake. Thus it is characterized by low alkalinity, and high sulphur and potassium.

Similar to that of Melchett Lake XRD analysis found no carbonate minerals present within rocks collected from the Briarcliff watershed. Coincidently results from the Kruskal- Wallis ANOVA test show that Briarcliff ranks second lowest in alkalinity concentrations, with only Melchett Lake ranked lower.

The Kruskal-Wallis ANOVA also illustrate that Briarcliff Lake ranks highest among lakes for Magnesium and Iron levels. When compared with final results from the column experiment, it appears consistent that Mg, and Fe levels in lake water appear to be influenced by surrounding geochemistry. The column from Briarcliff Lake finished the experiment with the highest concentration of Magnesium, and second highest level of Iron.

XRD analysis of geochemical composition of rocks from the Briarcliff Lake watershed show a number of Mg and Fe bearing minerals. Clinochlore, Flourannite, and Koninckite, were all found to be present in rock samples from Briarcliff Lake, all of which contain Mg and/or Fe. Hrnce these minerals are influencing Mg and Fe levels in Briarcliff Lake by chemical dissolution through a water/rock interaction.

Similar to Melchett Lake DFA picked out high potassium levels to discriminate Briarcliff from other lakes. Kruskal-Wallis ANOVA results coincide with this statement as lake water from Briarcliff ranked significantly higher in K concentrations when compared to the other study lakes. The main contributor of potassium to remote lakes are potassium bearing feldspars and micas. XRD analysis of rock samples from Briarcliff Lake illustrate that a variety of minerals containing K appear to be present. The minerals Fluorannite, Microcline, and Anorthoclase all contain K and were found throughout the sampling area. Thus the presence of these minerals in the watershed is influencing water chemistry throughout the aquatic system.

2.3.3 Esnagami Lake

Results from the discriminant function analysis suggest that Esnagami Lake is defined by high alkalinity, potassium and sulphur. Unlike other lakes thus far X-Ray diffraction found traces of dolomite in rock samples from Esnagami Lake. As mentioned earlier lake alkalinity is based on the presence of bicarbonates and carbonates and the $CO_2 - HCO_3^{-} CO_3^{2-}$ equilibrium system (Wetzel, 2001). Dolomite and calcite are commonly found carbonate minerals, and are the main minerals found in limestone and its metamorphic equivalent marble (Dyar et al. 2008). The presence and chemical dissolution of these minerals would undoubtedly increase alkalinity within the lake. The presence of dolomite within the watershed would most likely also attribute to the statistically higher ranks of calcium found within the lakes water samples, as the disassociation of carbonate minerals would increase concentrations of calcium to the lake.

In chapter 1, it was discussed that alkalinity inhibits mercury concentrations in aquatic systems, particularly in aquatic biota. Thus Walleye from Esnagami Lake were found to have the lowest mercury concentrations among all lakes sampled. The presence of dolomite and most likely calcite surrounding the lake may help control mercury concentrations within the fish population.

Results from both Kruskal-Wallis and the DFA both suggest that Sulphur concentrations are among the highest within Esnagami Lake. However when comparing final sulphur concentrations in the column experiment, rocks from Esngami leached some of lowest levels of sulphur into the water (final column concentration of 0.62mg/L). This suggests that not only did the rock contain no sulphide mineralization it also contained the lowest levels of trace native sulphur. This suggests that sulphur concentrations in Esnagami Lake maybe highly dependent on the aforementioned organic sulphides produced within surrounding wetlands or in lake production within shallow littoral zones and sediment. Another possibility maybe due to the vast size of Esnagami Lake in which only a small proportion of rock was sampled. Therefore isolated areas with higher levels of sulphur or sulphide minerals may have not been sampled, yet weathering of these rocks would contribute to levels in lake water.

Discrimanant function 1 from the DFA suggests that Esnagami is discriminated by low potassium levels. Results from the Kruskal-Wallis ANOVA suggest that K concentrations in Esnagami lake are neither the lowest or highest among lakes.. Regardless potassium is present at fairly significant concentrations in all data from Esnagami Lake. Similar to other lakes, the best explanation for the source of potassium, is the presence of K-bearing minerals. X-Ray diffraction analysis on rock samples from Esnagami Lake illustrates that Flourannite ($KFe_3 AlSi_3 O_{10} F_2$) was present in 2 of 3 samples. Weathering of rock containing this mineral would likely contribute potassium to the receiving waterbody

2.3.4 O'Sullivan Lake

Discrimination of water chemistry indicated that O'Sullivan closely followed that of Esnagami. Much like that of Esngami, O'Sullivan Lake ranked high compared to other lakes in regards of alkalinity. However unlike Esnagami, O'Sullivan Lake did not have any carbonate minerals present to contribute to alkalinity. However Ca concentrations ranked highest in O'Sullivan Lake. Results from the pairwise correlation from chapter 1 illustrated that calcium was highly correlated with alkalinity. This suggests that although no carbonate minerals were found in any of the samples, they still may be present within the watershed and contributing to alkalinity. Furthermore much like Esnagami, O'sullivan Lake is a vast waterbody, making it very possible to miss sections of rock containing carbonate during sampling. Similar to other lakes in the region, weathering of common minerals such as Albite that also contain Ca would further increase concentrations to the lake.

O'Sullivan Lake is also defined by high concentrations of S and low concentrations of K. The same processes (or a combination) explained previously most likely apply. When comparing results from the Kruskal-Wallis ANOVA, O'Sullivan Lake ranked very high in regards to numerous metal concentrations when compared with the other lakes. Included in this are the parameters iron, sodium, and aluminum.

Both high iron and aluminum concentrations in lake water maybe explained by the presence of the mineral Clinochlore $[(Mg\ Fe)6\ (Si\ Al)4\ O_{10}(OH)8]$. This particular mica was found in dominant proportions in all 4 rocks samples analyzed by XRD. Although the chemical weathering of micas are typically much slower then other minerals, the apparent abundance of Clinochlore in the area would likely contribute to iron and aluminum concentrations regardless of reaction rates. Furthermore the iron and aluminum bearing Koninckite $[(FeAl)\ PO_4 \cdot 3H_2O]$ was found in moderate proportions in one sample, which again may contribute to increasing levels in lake water. The felspar Albite $(Na_{0.98}\ Ca_{0.02})(Al_{1.02}\ Si_{2.98}\ O_8)$ which was found in moderate to dominate proportions in all samples also contains Al. Results from the column experiment agree with these suggestions as the O'Sullivan column some had some of the most dramatic increases of aluminum and iron concentrations.

Sodium concentrations were found to rank amongst the highest in O'Sullivan Lake compared to the other study lakes. The main source of Na to natural freshwaters is from the chemical weathering of sodium bearing felspars. Unlike potassium bearing felspars, felspars containing Na and Ca are more prone to chemical weathering (Hem, 1989). Again, Albite which was found in moderate to dominant proportions in all rock samples is most likely one of the largest contributors of Na to not only Esnagami Lake, but all study lakes.

2.3.5 Chaucer Lake

DFA found Chaucer Lake unique when compared to the other study lakes in regards to water chemistry. As Figure 2.0 displays Chaucer Lake clusters around the neutral mark of function 1 and significantly negative axis of function 2, signifying moderate alkalinity and potassium concentrations and low sulphur concentrations compared to the other lakes. When compared to the other lakes moderate potassium levels can be explained by the presence of the K-felspar mineral microcline in rock samples taken from the shoreline. K-felspars are sufficiently more resistant to chemical weathering then Ca-Mg felspars. If K-felspars are abundant in the area, the lake would most likely receive little K from these sources. Further evidence for this from the column experiment illustrates that very little calcium was leached from rock from Chaucer Lake in regards to the other columns. This suggests that K-felspars maybe predominant in the granitic rock from this area.

Chaucer Lake was also found to stand out in regards to the water/rock interaction experiments performed in the columns. As Table 2.7 indicates a number of the parameters displayed sharp increases initially on day 1 of sampling and then gradually decreased throughout the experiment. Parameters that followed this pattern included; Al, Ba, Ca, Cu, Fe, Mg, Na, Ni, S, Zn. Although other columns displayed similar reductions for some parameters, none had as many Chaucer. These reductions of concentrations over time maybe explained by changes of solubility. Solubility of metals in water is affected by numerous interacting factors. Oxidation or redox potential, pH, and activity of other ions within the water can all affect the solubility of metals within the column and on a larger scale within a lake (Hem, 1986)(Wagemann, R. 1978). Despite inability to pin-point what factor is influencing metal solubility within the Chaucer Lake column, evidently metal solubility decreased throughout the experiment causing metals to precipitate making them undetectable.

2.3.6 Mercury Study

The presence of sulphide minerals within surrounding lake geology should correspond to higher levels of mercury within the lake water and sediment. However XRD analysis found no sulphide bearing minerals within any of the samples. Even though no sulphide mineralization was found in XRD analysis, sulphides may have still been present at low concentrations. XRD analysis at Lakehead University's Instrumentation lab, detects minerals at approximately 5ppm. Minerals with low concentrations become overlapped by peaks of minerals with higher concentrations, and thus left out of analysis. This may explain the presence of S and Hg concentrations found throughout this experiment.

Mercury is also present in moderate levels as a trace metal in it elemental form in geological material surrounding the lakes. These results are consistent from similar studies. Rasmussen et al. (1998) found that bedrock rock and glacial tills similar to that found in the Aroland region in Huntsville, Ontario typically had low concentrations of Hg (5ppb). Results from the column experiment displayed that leaching of mercury is occurring from rocks in the region. However as Fig 2.5 illustrates mercury concentrations dramatically increased towards the latter part of the experiment, and appeared to still be increasing. This may be due to chemical changes within the columns, which increased the solubility of the Hg within the rocks. For example sudden decreases in pH within the columns would increase Hg mercury solubility and increase leaching from the rock, resulting in higher concentrations. Another explanation for the increases late in the experiment may be due to analytical or sampling errors during the experiment. Because detection limits of mercury analysis are so low, they are very prone to contamination, which could results in skewed data. Thus leaching of mercury from rock in the Aroland area most likely contributes only a small proportion the total Hg concentration of the aquatic systems. In order to make that available to aquatic biota, the Hg must be methylated. Thus regardless of the amount mercury added to a lake, methylation rates likely depict the amount of Hg that enters the food chain.

As found by Shilts and Coker, (1995), and Loukola-Ruskeeniemi (1990), large mercury anomalies in some lakes have been attributed to chemical weathering of black shales and sulphide bearing minerals. This does not appear to be case in the Aroland region. Therefore the most likely source of mercury to these remote lakes is from the abundance of surrounding wetlands in the area. As discussed in chapter 1, wetlands and in particular the amount of wetlands in a watershed influence mercury concentrations in the aquatic environments.

Conclusion

It was hypothesized that lake chemistry should influence and closely resemble that of the geochemistry of the surrounding watershed. For the most part rocks found within each watershed were typical of that found in the Boreal forest; granites consisting of mostly quartz, numerous types of feldspars (in particular Albite) and micas. It is feldspars and to a lesser extent micas that contribute a large proportion of K, Mg, and Ca to lakes in this particular region. Furthermore XRD analysis found that lakes (in particularly O'Sullivan Lake) with predominantly more minerals bearing elements such as iron and sodium typically had higher concentrations of the elements, indicating the influential role local geology plays.

Local geology also influenced alkalinity in the study lakes. Lakes situated in or close proximity to carbonate bearing rock will typically have much higher alkalinities. Study lakes within the Aroland region follow this pattern as Esnagami, the only lake found with carbonate minerals present had the highest rank of alkalinity when compared to the other lakes without carbonates. Esnagami lake was also found to have the highest rank of Ca concentration, due to the presence of the Dolomite within the watershed. Thus elevated alkalinity and to a lesser extent calcium in Esngami lake can be attributed to the influence by surrounding geochemistry.

Although it is difficult to quantify the exact extent watershed geology plays in lake water chemistry it does appear to play an important role.

The presence of sulphide mineralization elevates levels of mercury within receiving lakes. Although XRD demonstrated that no sulphides were found to be present in any rocks samples taken from the study area, water/rock interaction experiments prove that leaching of Hg from surrounding rock still occurs in small quanitities. Such processes add to total mercury concentrations to a lake system, and under the proper conditions for methylation can increase mercury concentrations in aquatic biota.

However most of the mercury added to the Aroland lakes come from wetlands in the area.

2.4 General Conclusion and Implications

Like many before it, studies such this exemplify the complex nature of mercury contamination, and to a certain extent other toxins, The level of contamination is often associated with the interaction of a number of chemical, spatial, and biological factors. I found that the chemical characteristics and general health of remote lakes is due to a number of externals factors. In particularly important was wetland abundance and geochemistry of the surrounding watershed. Furthermore fluctuations of chemical constituents affected the levels of other parameters within individual lakes. This is best documented by the positive and negative relationships found between dissolved organic carbon and alkalinity in regards to THg concentrations in fish tissues from.

Both natural and anthropogenic disturbance and their abilities to change water chemistry can increase levels of Hg within aquatic systems. Such studies will prove invaluable with the development of the “Ring of Fire” in Ontario’s remote far north. The “Ring of Fire” is a 5120km^2 area of land being touted as one of the richest chromite ore deposits on Earth. Furthermore economical quantities of copper sulphide and other significant ore mineralization have also been found to be present (Reynolds, 2008).

Much of the deposit is situated underneath the peatlands and wetlands of the Hudson Bay Lowlands. With the development of open pit mines and mining infrastructure the area will undoubtedly be disrupted and the natural function of countless pristine lakes and streams affected. Without proper planning removal and harvesting the wetlands will drastically release and increase levels of DOC to surrounding lakes and streams. As found in this study large fluxes of DOC to an aquatic system can potentially increase levels of mercury within them. Furthermore the oxidation of sulphide minerals and leaching of rock tailing piles have the potential to alter pH levels through acid mine drainage and increase the solubility of a variety of metals. Without proper management the transport of these leachates to aquatic systems, could have serious detrimental effects on both aquatic and terrestrial biota.

The scientific knowledge gained in studies such as these can form the basis of environmental management for large-scale operations such as the Ring of Fire. Having the ability to predict the interactions and potential consequences involved with mining before they occur, allows managers to mitigate and minimize the amount of environmental damage.

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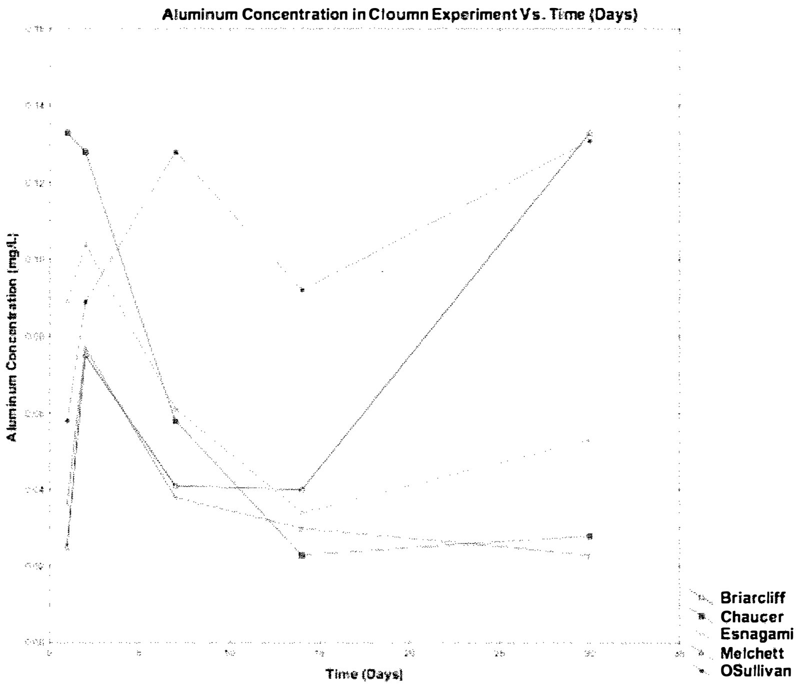
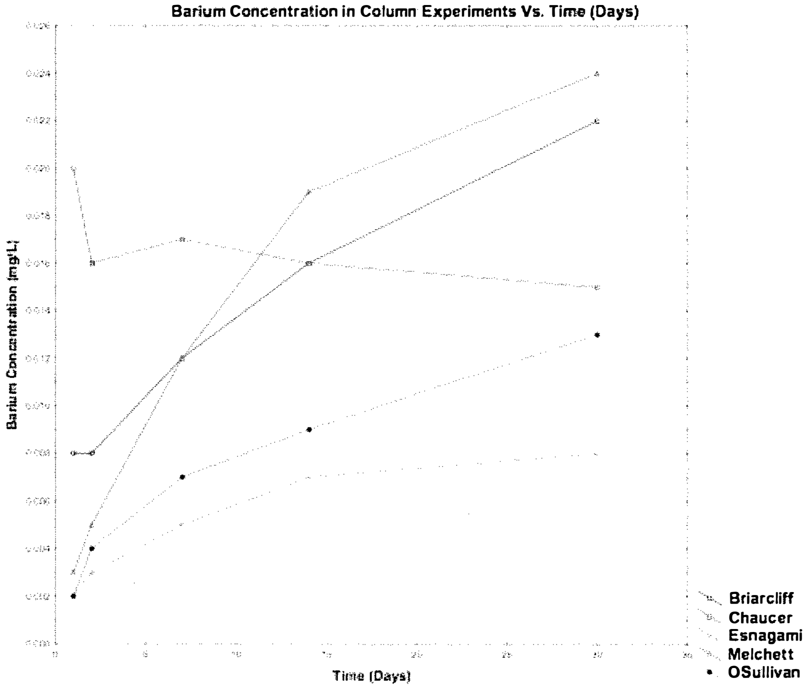
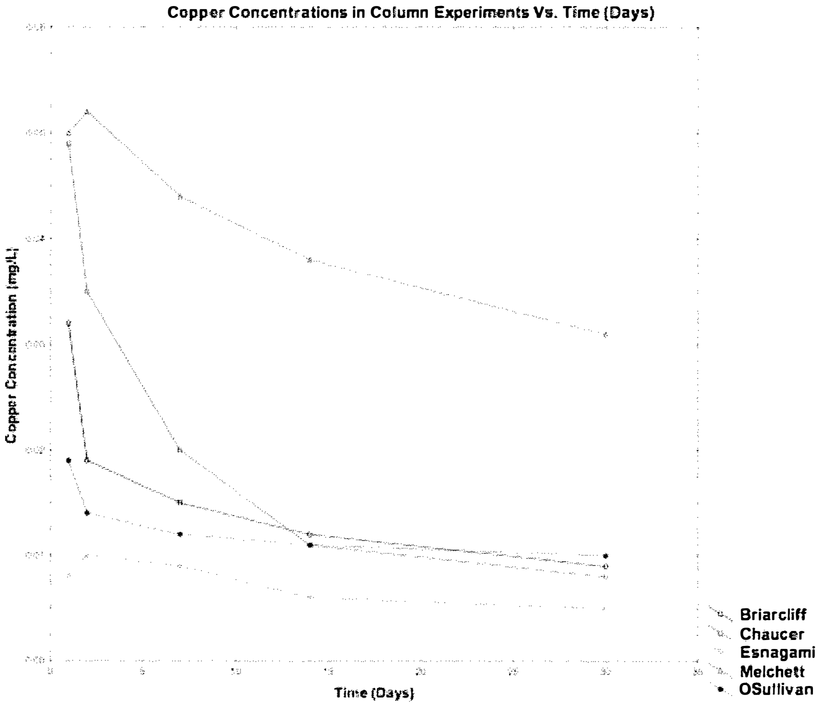
Appendix 1. Complete Results from Water/Rock Column Interaction Experiments



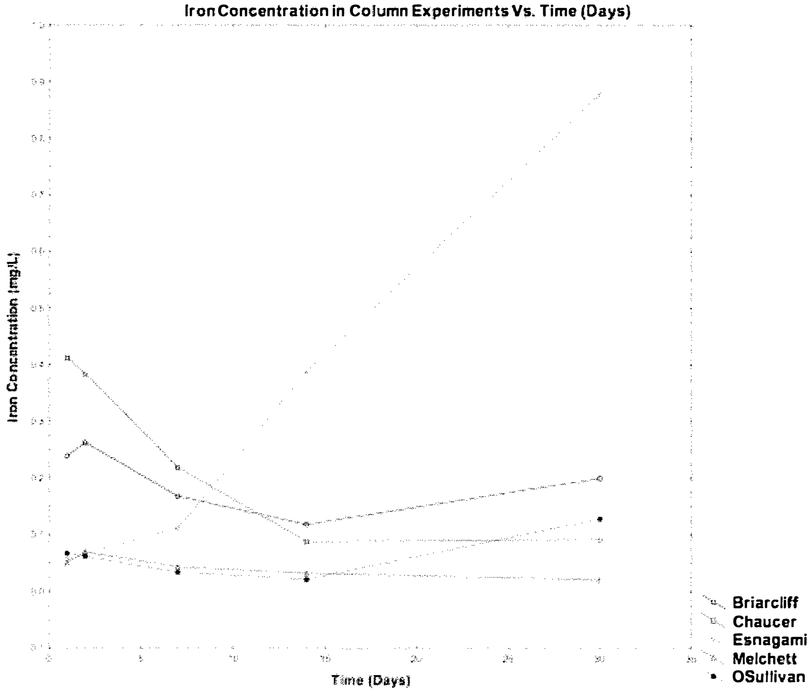
Aluminum



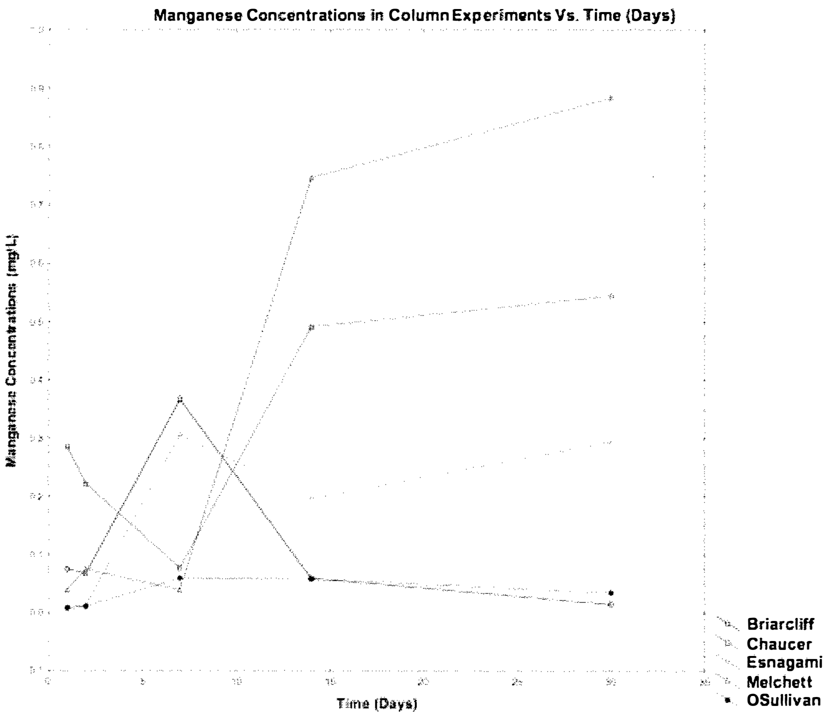
Barium


Copper Concentrations in Column Experiments Vs. Time (Days)
Copper Concentration (mg/L)
Time (Days)
0
5
10
15
20
25
30
35
Briarcliff
Chaucer
Esnagami
Melchett
OSullivan

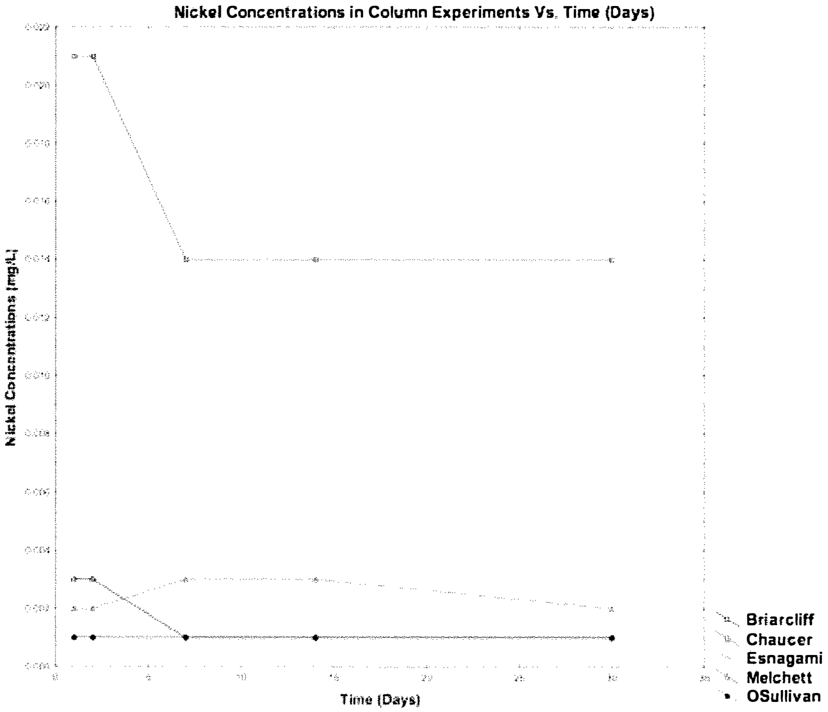
Copper


Iron Concentration in Column Experiments Vs. Time (Days)
Iron Concentration (mg/L)
Time (Days)
0
5
10
15
20
25
30
35
Briarcliff
Chaucer
Esnagami
Melchett
OSullivan

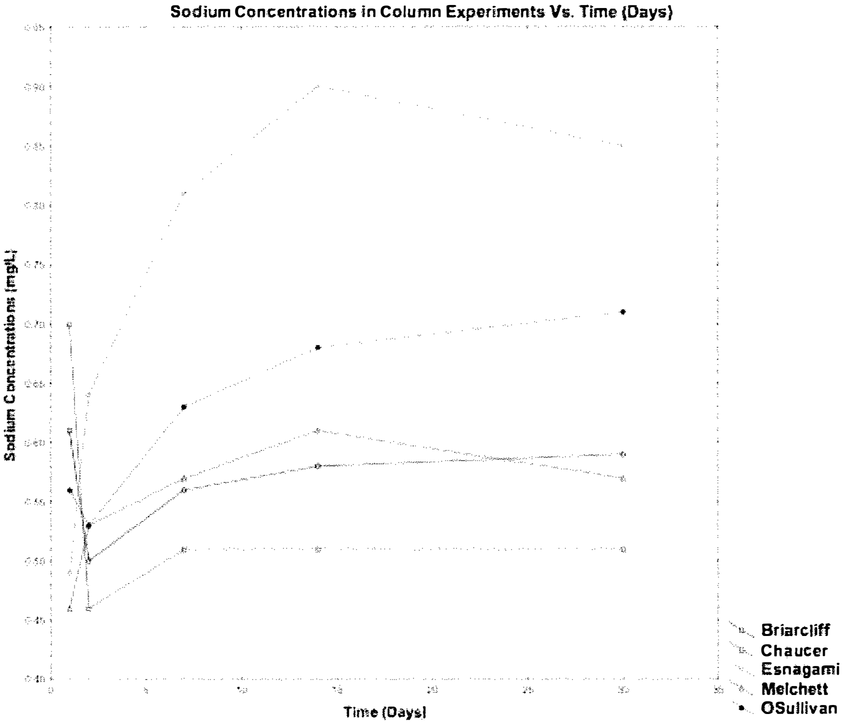
Iron



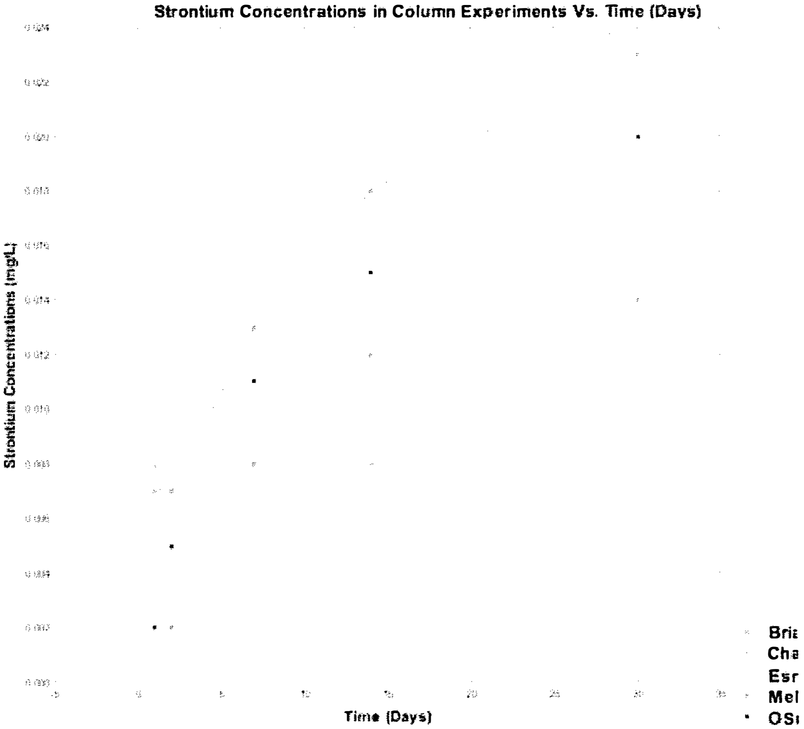
Manganese



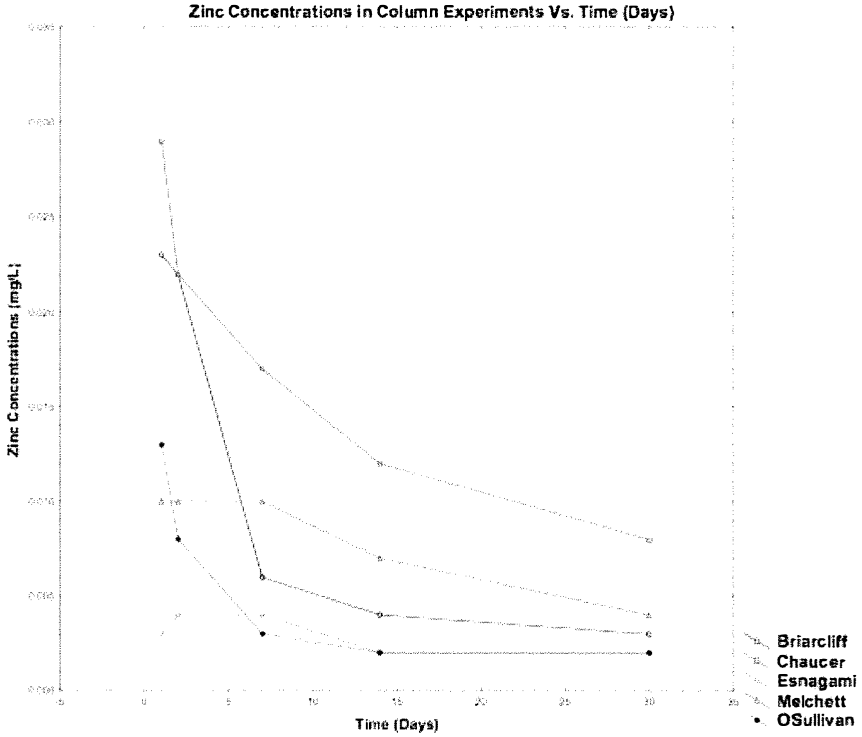
Nickel



Sodium



Strontium

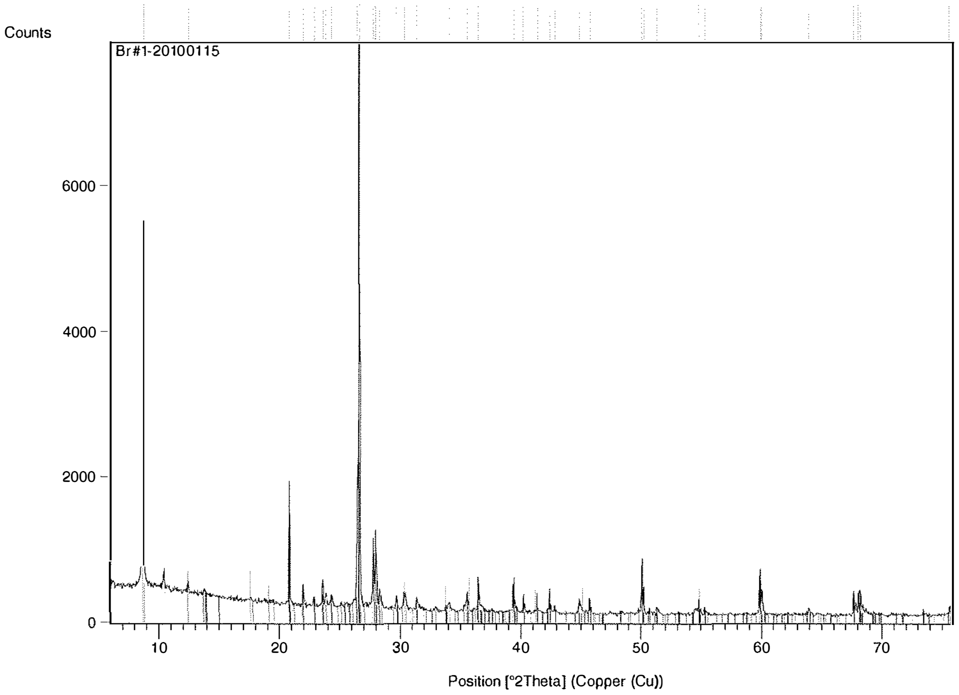

Zinc Concentrations in Column Experiments Vs. Time (Days)
Zinc Concentrations (mg/L)
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-5
0
5
10
15
20
25
30
35
Time (Days)
Briarcliff
Chaucer
Esnagami
Melchett
OSullivan

Zinc

Appendix 2. Complete Results from XRD Analysis

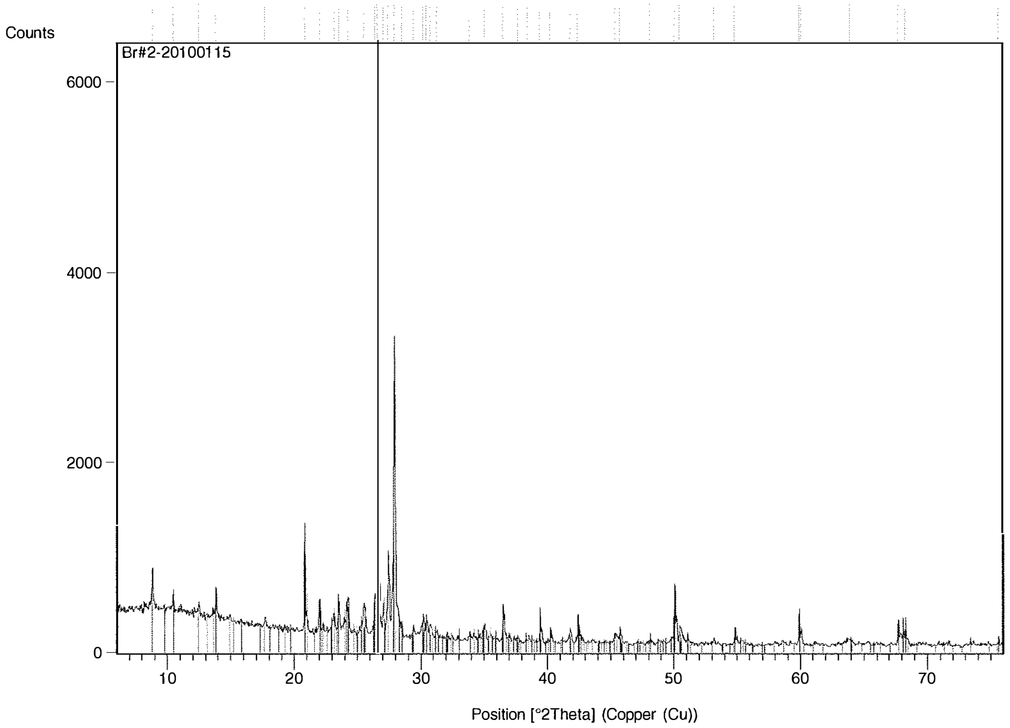
Briarcliff Lake

Sample #1



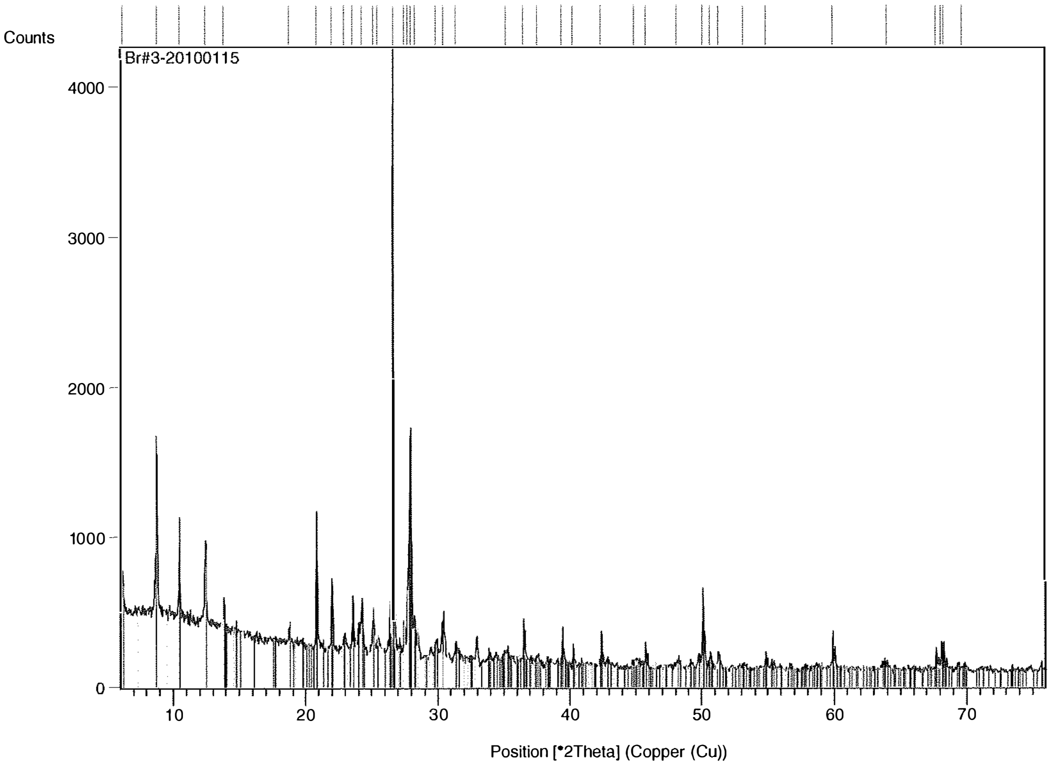
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-087-2096	75	á-Si O2	-0.005	0.987	Si O2
*	00-041-1480	39	Albite, calcian, ordered	-0.016	0.131	(Na , Ca) Al (Si , Al)3 O8
*	00-053-1188	22	Fluorannite	-0.020	0.438	K Fe3 Al Si3 O10 F2
*	00-037-0473	7	Hauyne	0.077	0.015	Na6 Ca2 Al6 Si6 O24 (S O4)2
*	01-079-2176	21	Wustite, syn	-0.044	0.033	Fe.922 O
*	00-046-0362	7	Copper Vanadium Oxide	-0.170	0.035	Cu1.3 V9 O22

Sample #2



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-083-2465	68	silicon dioxide	0.000	0.834	Si O2
*	00-009-0466	38	Albite, ordered	0.000	0.228	Na Al Si3 O8
*	00-022-0687	35	Microcline, ordered	0.000	0.117	K Al Si3 O8
*	01-080-1286	14	Rho, strontium cesium tecto-alumosilicate	0.000	0.064	Sr4.0 Cs1.1 (Al12 Si36 O96)
*	00-020-0469	14	Hastingsite, magnesian	0.000	0.033	(Ca , Na)2 (Fe2 , Mg)5 (Si , Al)8 O22 (O H)2

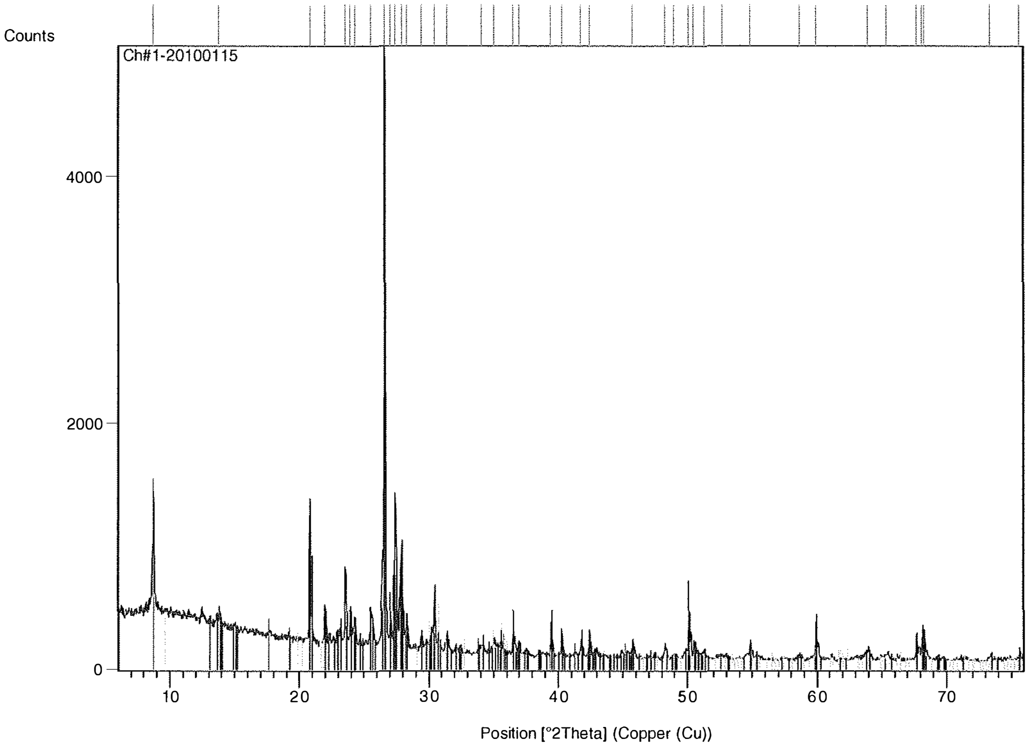
Sample #3



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-087-2096	68	á-Si O2	0.000	0.991	SiO_2
*	00-041-1480	45	Albite, calcian, ordered	0.000	0.317	$(Na, Ca)Al(Si, Al)_3O_8$
*	00-029-0701	36	Clinochlore-1MIIb, ferroan	0.000	0.115	$(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$
*	01-074-1758	14	Dickite	0.000	0.276	$Al_2Si_2O_5(OH)_4(HCONH_2)$
*	00-022-0339	21	Koninckite	0.000	0.156	$(Fe, Al)PO_4 \cdot 3H_2O$
*	00-009-0478	21	Anorthoclase, disordered	0.000	0.097	$(Na, K)(Si_3Al)O_8$

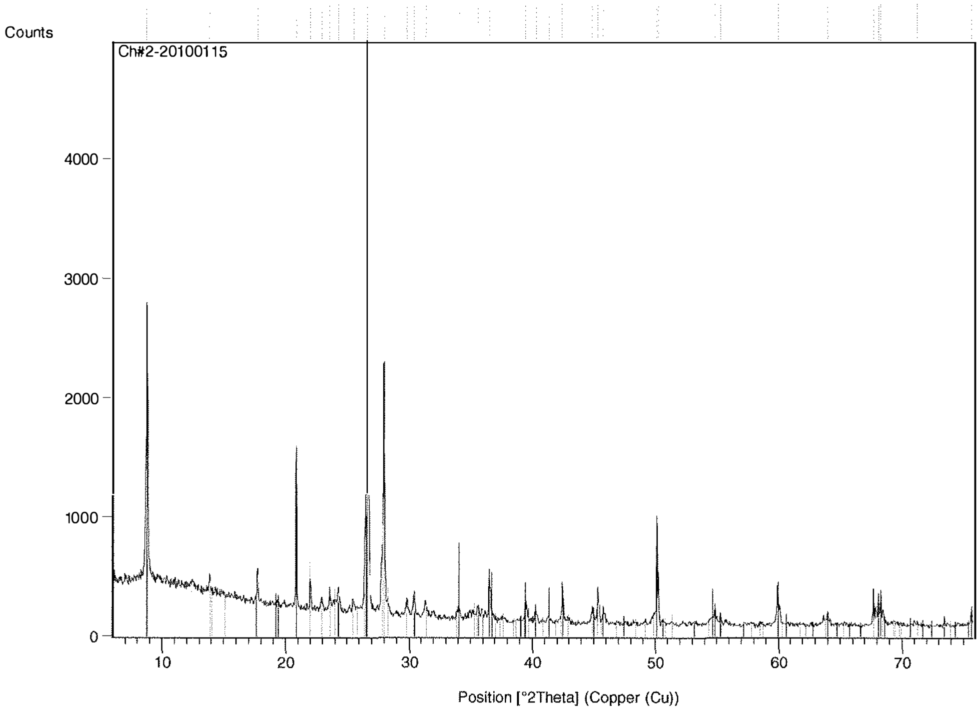
Chaucer Lake

Sample #1



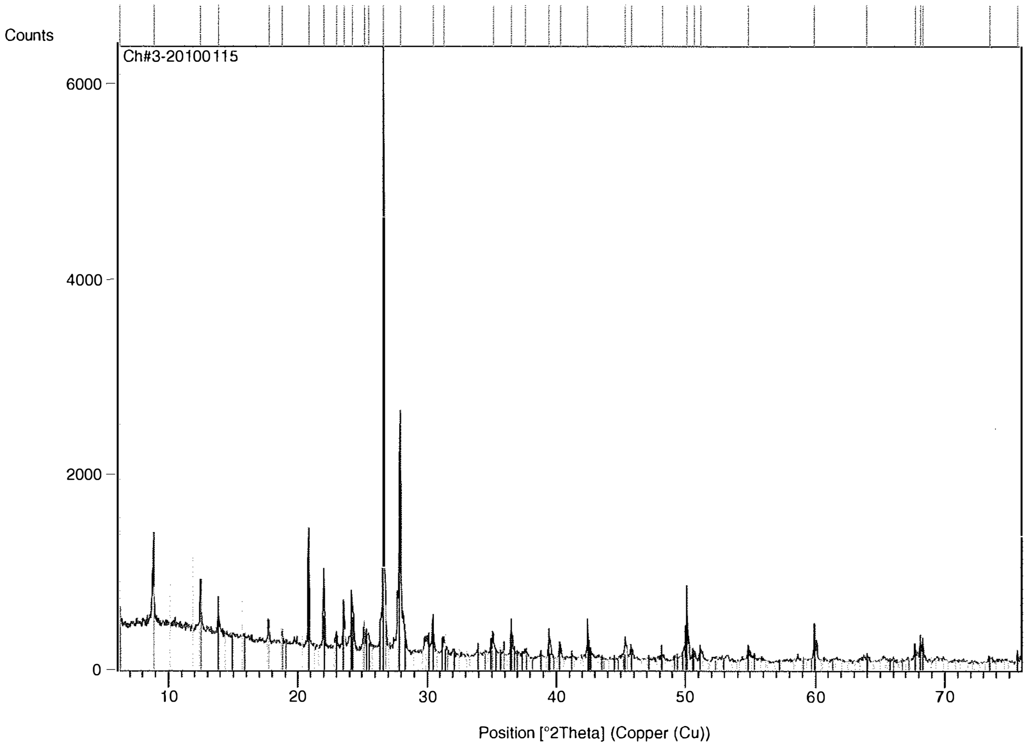
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-085-0797	71	Quartz, syn	0.000	1.004	SiO_2
*	00-041-1480	36	Albite, calcian, ordered	0.000	0.169	$(Na, Ca)Al(Si, Al)_3O_8$
*	00-053-1188	26	Fluorannite	0.000	0.386	$KFe_3AlSi_3O_{10}F_2$
*	00-019-0926	32	Microcline, ordered	0.000	0.137	$KAlSi_3O_8$

Sample #2



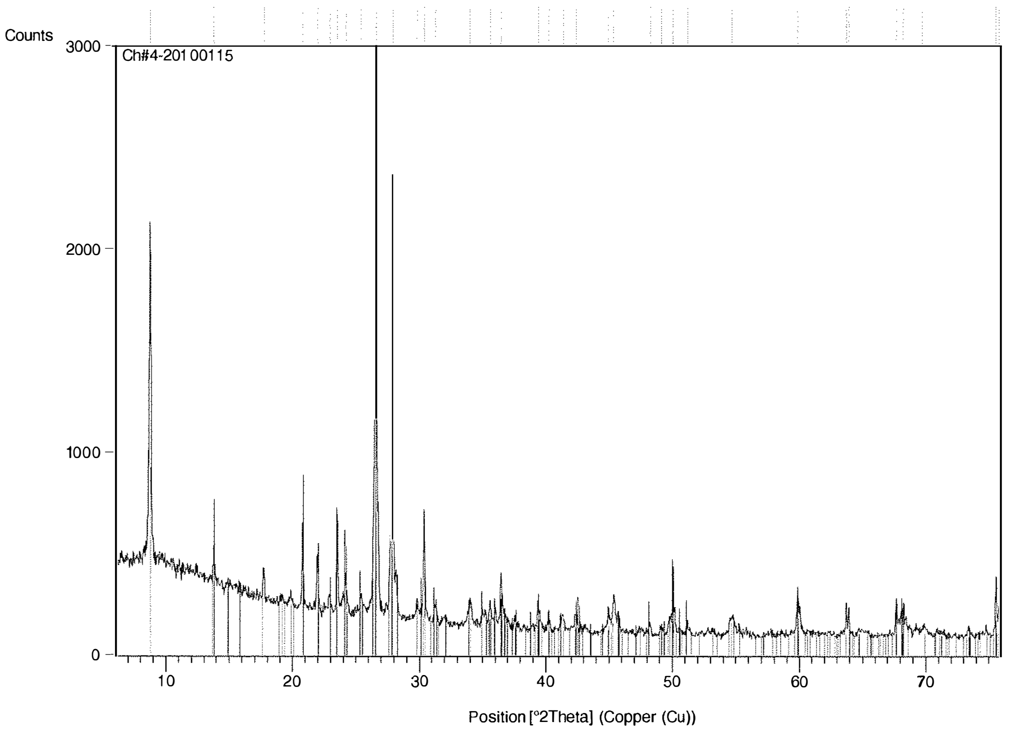
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-083-2465	72	silicon dioxide	0.000	1.024	SiO_2
*	00-042-1437	38	Phlogopite-1M, ferroan	0.000	0.444	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$
*	00-041-1480	34	Albite, calcian, ordered	0.000	0.288	$(Na,Ca)Al(Si,Al)_3O_8$

Sample #3



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	03-065-0466	68	Quartz low, syn	0.000	1.002	O2 Si
*	00-009-0466	41	Albite, ordered	0.000	0.301	Na Al Si3 O8
*	00-029-0701	34	Clinochlore-1MIIb, ferroan	0.000	0.073	(Mg , Fe)6 (Si , Al)4 O10 (O H)8
*	00-058-2016	27	Illite-2M2, glycolated	0.000	0.066	(K , H30) Al2 (Si3 Al) O10 (O H)2 ·x H2 O

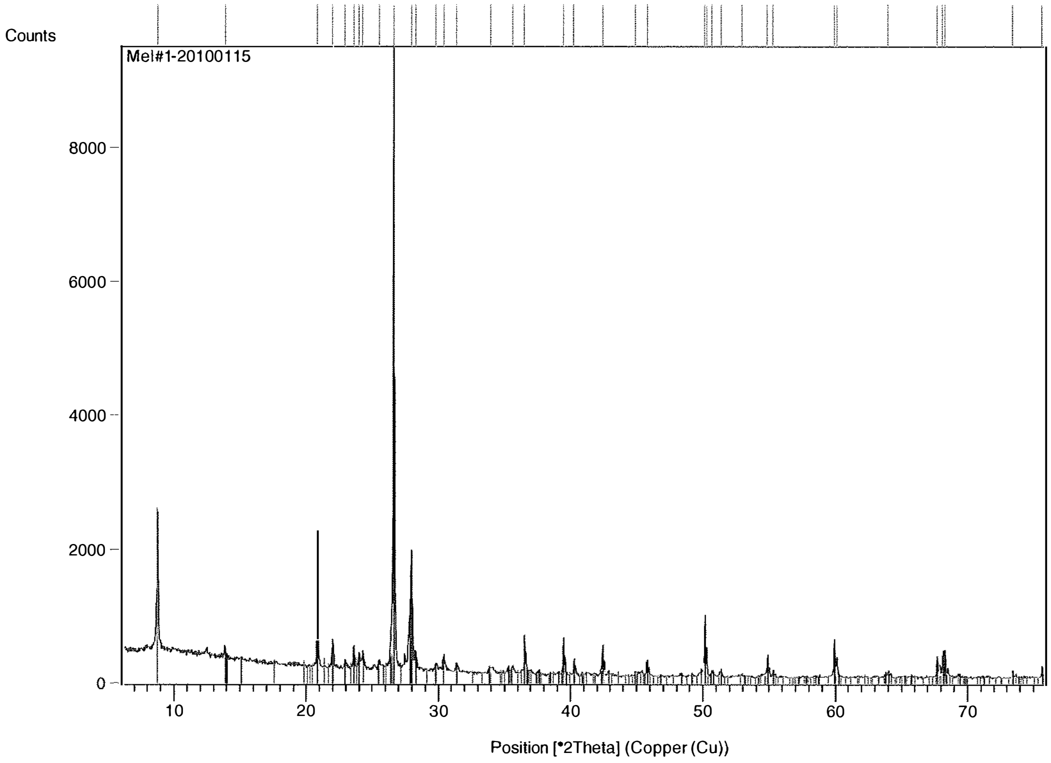
Sample #4



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-078-1252	60	á-Si O2, quartz low high HP, syn	0.000	0.981	Si O2
*	00-009-0466	37	Albite, ordered	0.000	0.675	Na Al Si3 O8
*	00-042-1437	39	Phlogopite-1M, ferroan	0.000	0.593	K (Mg , Fe)3 (Al , Fe) Si3 O10 (O H , F)2
*	01-075-1092	12	calcium magnesium catena-silicate	0.000	0.134	Ca Mg Si2 O6

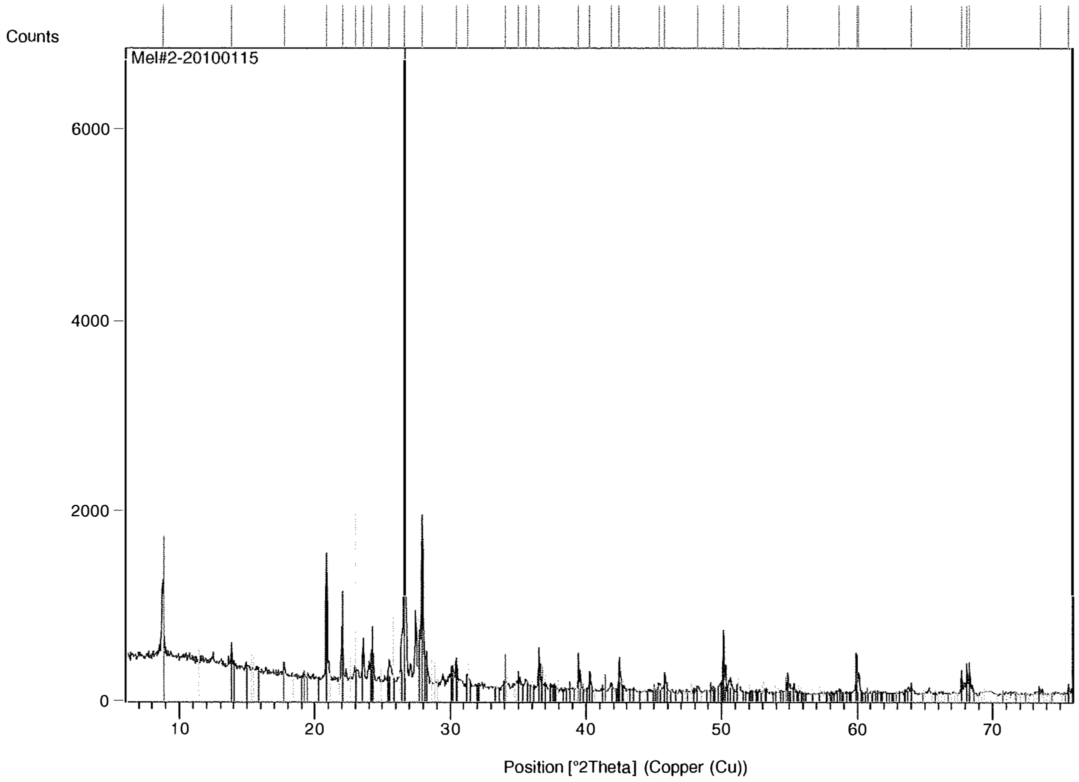
Melchett Lake

Sample #1



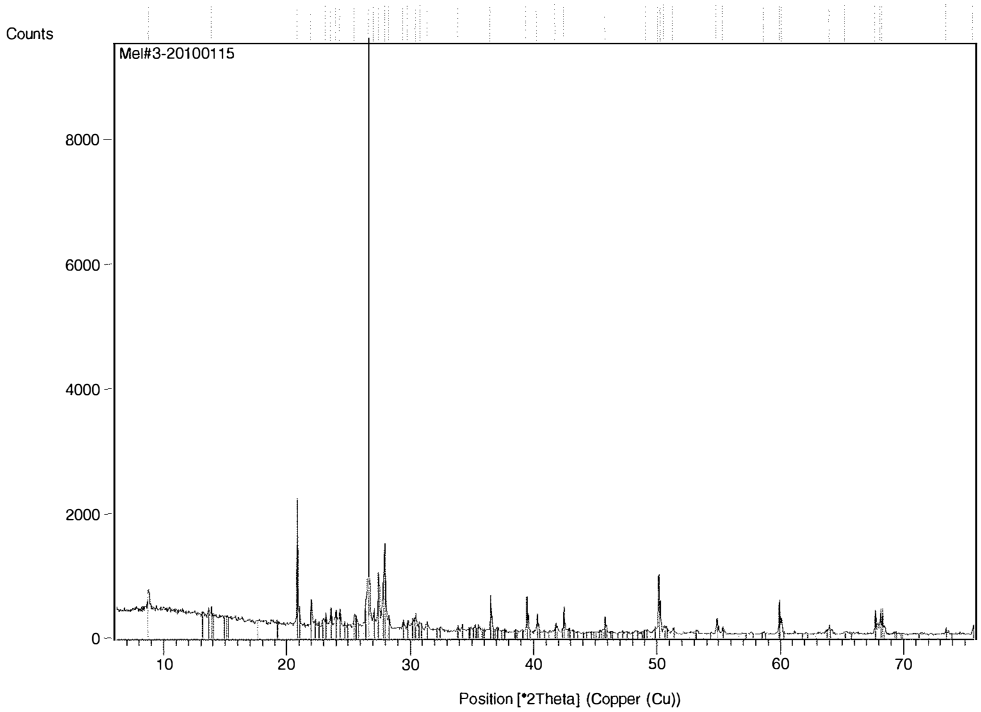
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-087-2096	80	á-Si $\mathrm{O_2}$	0.000	0.986	$\mathrm{Si\ O_2}$
*	00-041-1480	46	Albite, calcian, ordered	0.000	0.156	$\mathrm{(\ Na\ ,\ Ca\ )\ Al\ (\ Si\ ,\ Al\ )_3\ O_8}$
*	01-074-1758	24	Dickite	0.000	0.224	$\mathrm{Al_2\ Si_2\ O_5\ (\ O\ H\ )_4\ (\ H\ C\ O\ N\ H_2\ )}$

Sample #2



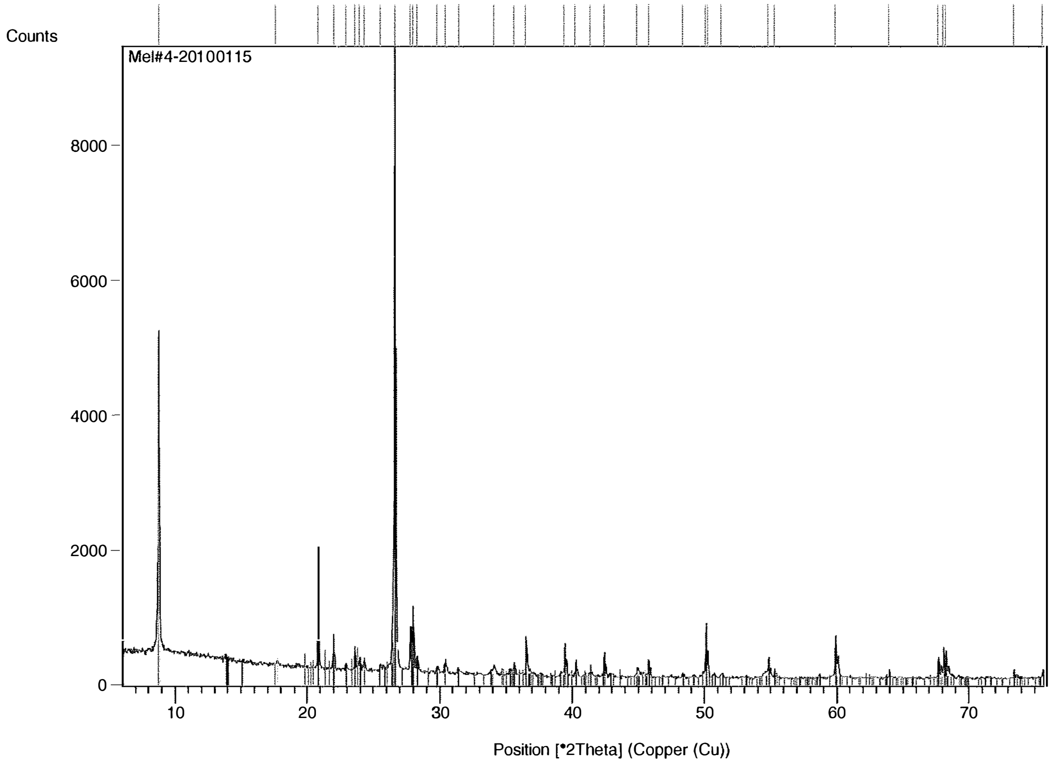
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-083-2465	75	silicon dioxide	-0.011	0.853	SiO_2
*	01-070-3752	36	Albite	0.005	0.196	$(Na_{0.98}Ca_{0.02})(Al_{1.02}Si_{2.98}O_8)$
*	00-042-1437	22	Phlogopite-1M, ferroan	0.047	0.213	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$

Sample #3



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-087-2096	76	á-Si O2	0.000	0.985	Si O2
*	00-041-1480	36	Albite, calcian, ordered	0.000	0.125	(Na , Ca) Al (Si , Al)3 O8
*	00-053-1188	22	Fluorannite	0.000	0.227	K Fe3 Al Si3 O10 F2
*	00-022-0687	23	Microcline, ordered	0.000	0.061	K Al Si3 O8

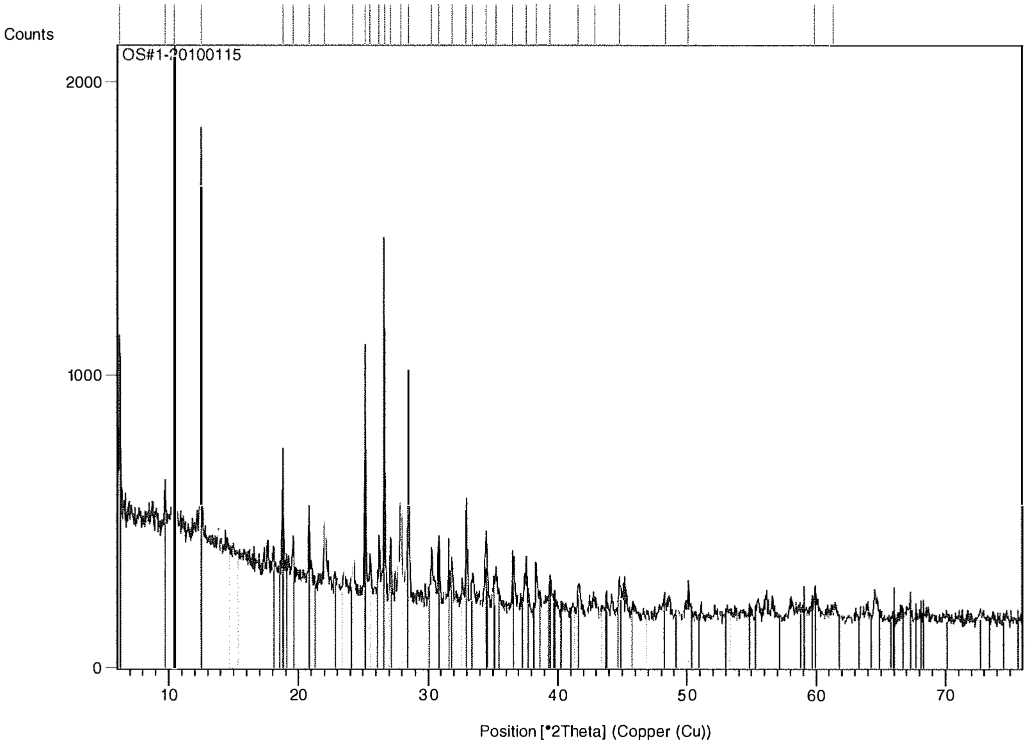
Sample #4



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-087-2096	78	á-Si O2	0.000	0.983	Si O2
*	00-041-1480	41	Albite, calcian, ordered	0.000	0.099	(Na , Ca) Al (Si , Al)3 O8
*	01-074-1758	25	Dickite	0.000	0.443	Al2 Si2 O5 (O H)4 (H C O N H2)
*	01-079-1969	25	Wustite, syn	0.000	0.027	Fe.920 O

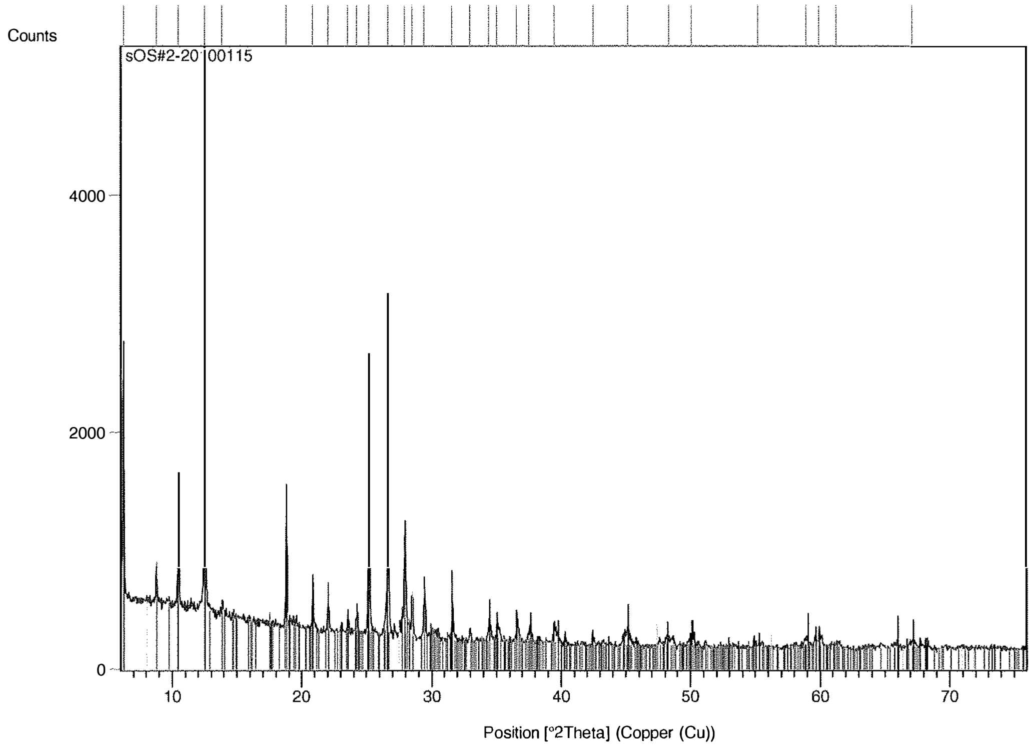
O’Sullivan Lake

Sample #1



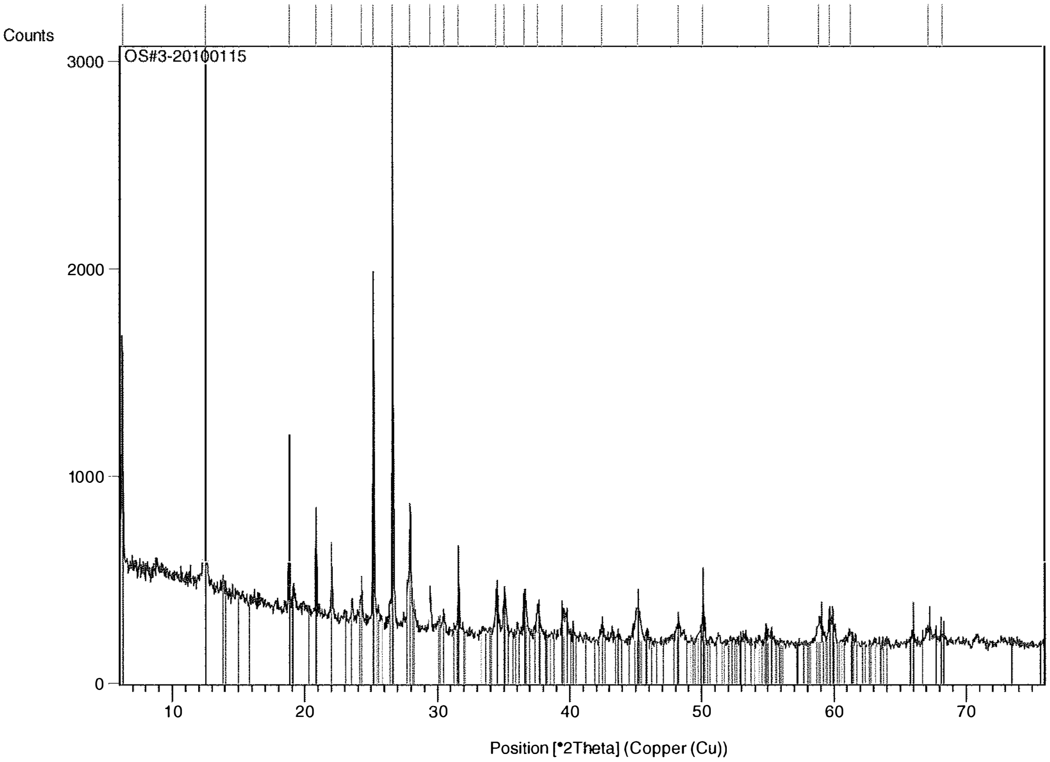
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-029-0701	48	Clinochlore-1MIIb, ferroan	0.012	0.681	$(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$
*	01-070-3755	40	Quartz	0.011	0.550	SiO_2
*	01-070-3752	18	Albite	0.027	0.186	$(Na_{0.98}Ca_{0.02})(Al_{1.02}Si_{2.98}O_8)$
*	00-012-0088	19	Ankerite	0.026	0.126	$Ca(Mg_{0.67}Fe_{0.33}^{+2})(CO_3)_2$
*	00-023-0603	36	Previously called tirodite, tirodite	-0.056	0.599	$(Na, Ca)_2(Mg, Mn, Fe)_5Si_8O_{22}(OH)_2$

Sample #2



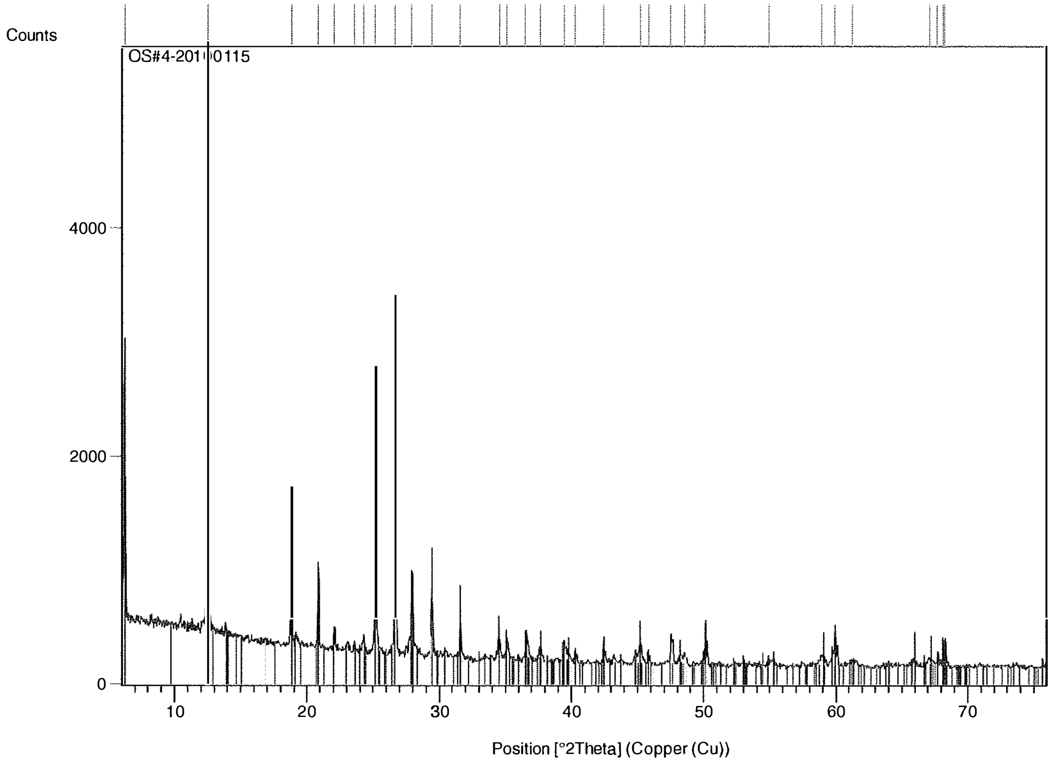
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-029-0701	53	Clinochlore-1MIIb, ferroan	0.004	0.721	(Mg , Fe)6 (Si , Al)4 O10 (O H)8
*	01-085-0795	49	Quartz, syn	-0.035	0.285	Si O2
*	01-073-9211	19	Carlinite	0.068	0.105	Tl2 S
*	01-070-3752	26	Albite	0.009	0.120	(Na0.98 Ca0.02) (Al1.02 Si2.98 O8)
*	00-022-0339	22	Koninckite	-0.030	0.200	(Fe , Al) P O4 ·3 H2 O
*	01-073-6559	15	Marmetite	-0.047	0.069	Zn0.73 Fe0.27 S
*	01-076-1675	9	Serpierite	0.117	0.093	Ca (Cu0.66 Zn0.34)4 (O H)6 (S O4)2 (H2 O)3

Sample #3



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	03-065-0466	63	Quartz low, syn	0.000	0.967	$O_2 Si$
*	00-029-0701	73	Clinochlore-1MIIb, ferroan	0.000	0.896	$(Mg , Fe)_6 (Si , Al)_4 O_{10} (O H)_8$
*	01-070-3752	21	Albite	0.000	0.173	$(Na_{0.98} Ca_{0.02}) (Al_{1.02} Si_{2.98} O_8)$
*	01-073-9211	8	Carlinite	0.000	0.041	$Tl_2 S$

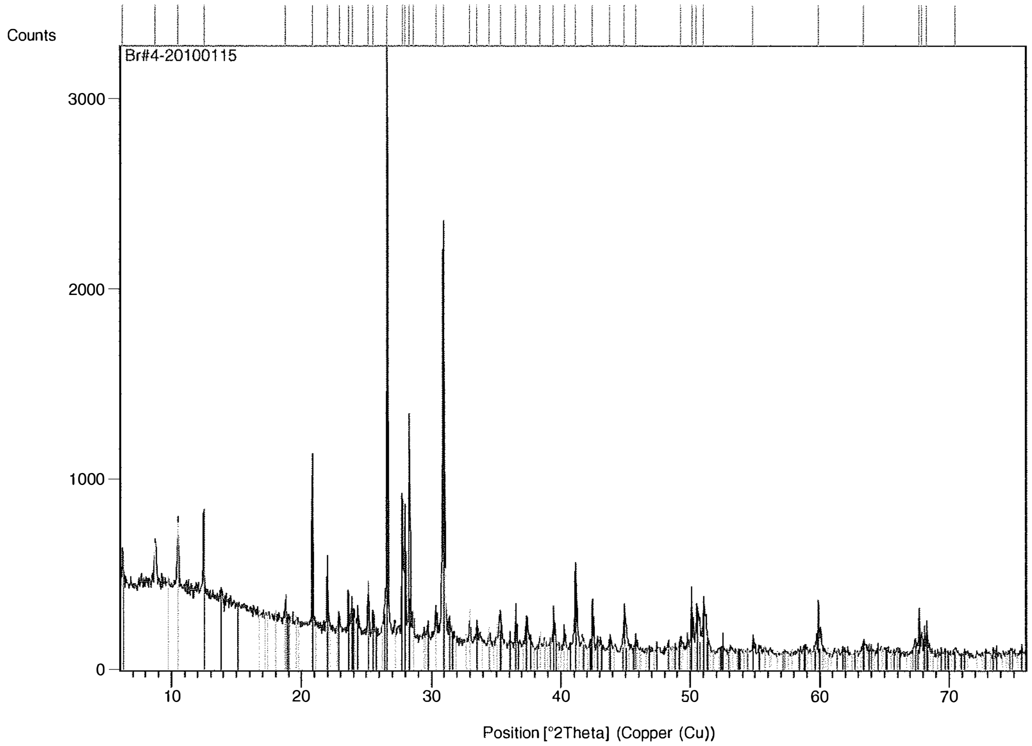
Sample #4



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-085-0504	60	Quartz	-0.008	0.316	Si O2
*	00-029-0701	54	Clinochlore-1MIIb, ferroan	0.007	0.736	(Mg , Fe)6 (Si , Al)4 O10 (O H)8
*	01-073-9211	15	Carlinite	0.063	0.126	Tl2 S
*	00-041-1480	17	Albite, calcian, ordered	-0.015	0.090	(Na , Ca) Al (Si , Al)3 O8

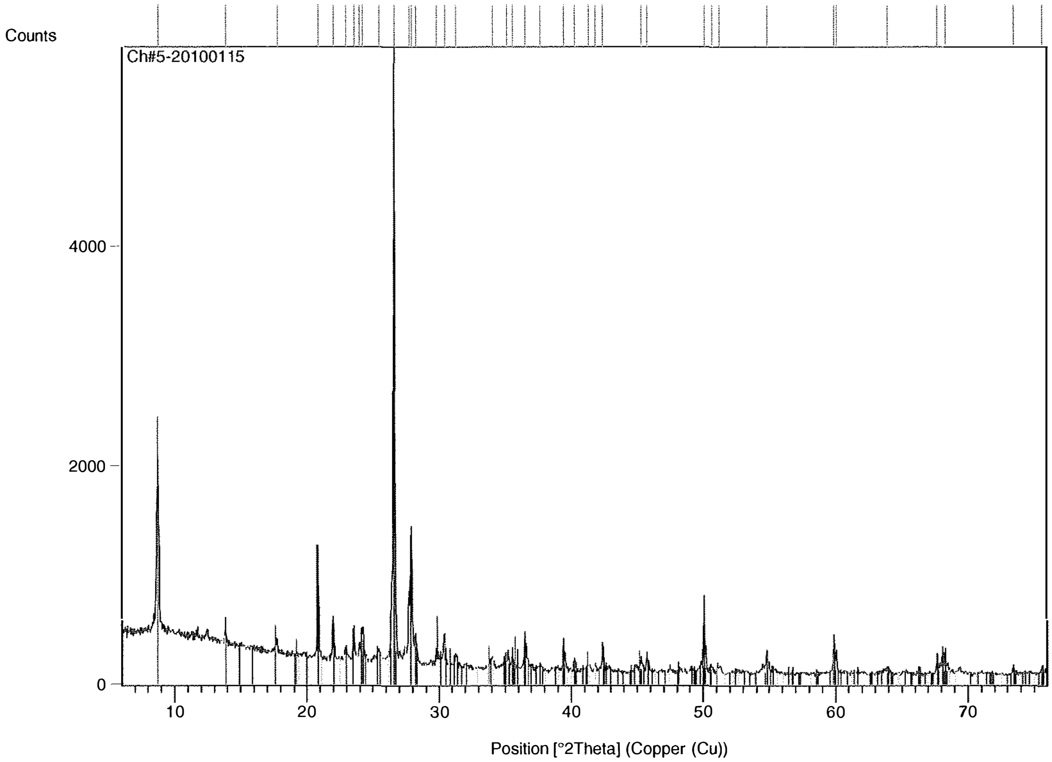
Esnagami Lake

Sample #1



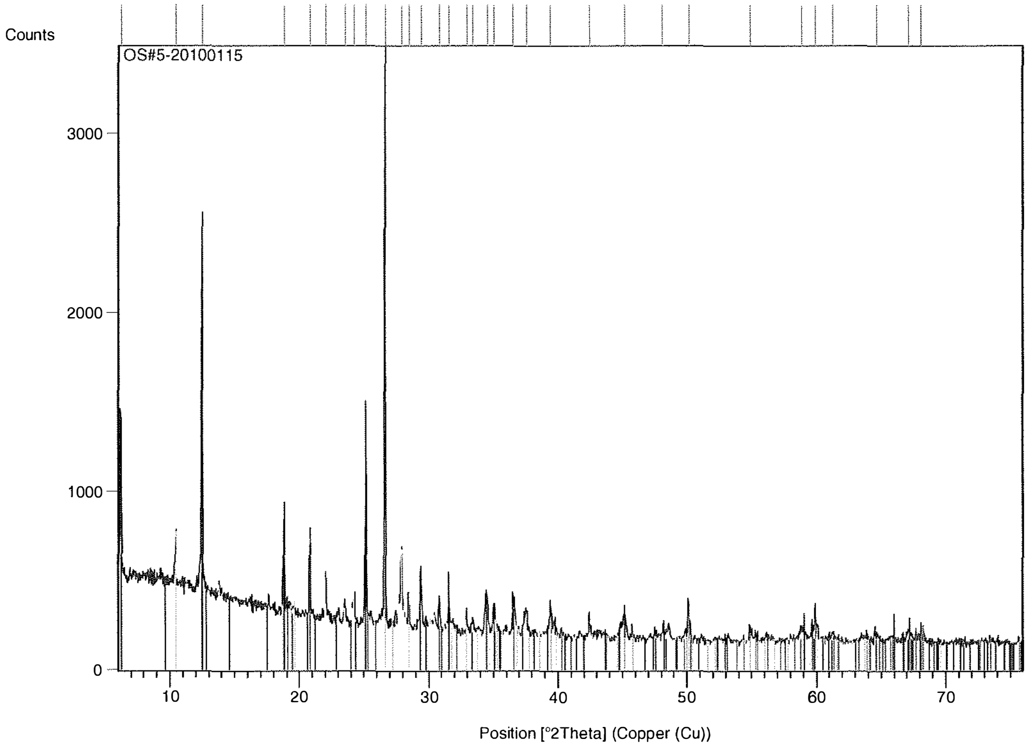
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-070-3755	64	Quartz	0.000	1.016	Si O2
*	00-036-0426	56	Dolomite	0.000	0.669	Ca Mg (C O3)2
*	00-029-0701	30	Clinochlore-1MIIb, ferroan	0.000	0.138	(Mg , Fe)6 (Si , Al)4 O10 (O H)8
*	00-020-0548	29	Albite, calcian, ordered	0.000	0.224	(Na , Ca) (Si , Al)4 O8
*	00-053-1188	29	Fluorannite	0.000	0.267	K Fe3 Al Si3 O10 F2
*	01-071-0688	10	Ferrotschermakite	0.000	0.105	(Na.23 K.14 Ca1.86) (Mg1.22 Fe2.10 Mn.02 Ti.10 Fe.30 Al1.30) Al2 Si6 O22 (O H)2

Sample #2



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	03-065-0466	66	Quartz low, syn	0.000	0.997	$O_2 Si$
*	00-009-0466	38	Albite, ordered	0.000	0.188	$Na\,Al\,Si_3\,O_8$
*	00-053-1188	38	Fluorannite	0.000	0.427	$K\,Fe_3\,Al\,Si_3\,O_{10}\,F_2$
*	01-086-0002	11	magnesium iron calcium sodium catena-disilicate	0.000	0.075	$(Mg_{0.930}\,Fe_{0.070})(Ca_{0.770}\,Na_{0.214}\,Fe_{0.016})(Si_{1.78}\,Al_{0.22}\,O_6)$
*	00-009-0478	18	Anorthoclase, disordered	0.000	0.072	$(Na, K)(Si_3\,Al)O_8$

Sample #3



Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-087-2096	60	á-Si O2	0.000	0.982	Si O2
*	00-029-0701	61	Clinochlore-1MIIb, ferroan	0.000	0.592	(Mg , Fe)6 (Si , Al)4 O10 (O H)8
*	01-073-9211	11	Carlinite	0.000	0.092	Tl2 S
*	01-070-3752	20	Albite	0.000	0.119	(Na0.98 Ca0.02) (Al1.02 Si2.98 O8)
*	00-012-0088	17	Ankerite	0.000	0.042	Ca (Mg0.67 Fe0.33 +2) (C O3)2
*	00-009-0436	16	Riebeckite	0.000	0.122	Na2 Fe3 Fe2 Si8 O22 (O H)2