Lake sediment geochemistry in northeastern Ontario;
the geologic controls on natural background variation
and investigating lakes contaminated with arsenic-
rich mine tailings in Cobalt, ON.

Submitted by
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Tailings and waste rock at Kerr Lake, Cobalt, ON.

Abstract

This thesis investigates lake sediment geochemistry from regions in Northeastern Ontario from the areas around Gowganda, Temagami and Cobalt. The environmental legacy of the Cobalt mining camp represents an area that has been extremely impacted by arsenic-rich mine waste. The primary objectives of this thesis were to determine the magnitude and spatial extent of arsenic contamination in Cobalt, ON, and to determine realistic background concentrations of arsenic for the region. To aid in this investigation, in Chapter 3 I examined adjacent areas of Temagami and Gowganda, using historical lake sediment records collected by the Ontario Geological Survey (OGS) (Hamilton, 1997; Takats and Dyer, 2004) to determine background geochemical and arsenic concentrations over a much larger spatial scale in an effort to establish controlling factors influencing lake sediment geochemistry, under similar geological, biological, and climatic conditions. This chapter highlighted that bedrock geology is an important control on lake sediment geochemistry and that specific geochemical assemblages can be spatially associated to specific bedrock types. Additionally, lake catchments with different bedrock geology displayed differing background levels for metals and, notably, the Nipissing Diabase being highly correlated to areas that displayed elevated geochemical signatures for Cobalt-type mineralization. In Chapter 4, the current contaminant levels in lake sediments and surface waters in Cobalt and Silver Center mining camps were determined. In contaminated lakes, mine tailings on the lake bottom were found to contain up to 10,800 mg/kg of arsenic, which is 635 times the objective for the protection of aquatic life and 981 times the mean value found in control lakes (11 mg/kg). However, tailings in contaminated lakes were typically in the 1000 - 3000 mg/kg range. Surface waters in

contaminated lakes also contained extremely alarming amounts of arsenic, up to 972 µg/L which is 97 times the drinking water standard of 10 µg/L and 194 times the 5 µg/L objective for the protection of aquatic life. The mean arsenic concentration in contaminated lakes was substantially lower (431 mg/kg) but still 86 times the 5 µg/L objective for the protection of aquatic life. Three methods for determining background arsenic concentrations were applied using control lakes from Cobalt, data from Chapter 3, and sampling below tailings in contaminated lakes, and a reasonably flexible background range of 100-200 mg/kg was determined. The study also showed that on-going tailings migration and surface waters flowing from contaminated catchments can substantially impact lakes downstream that had no mining activity in their watershed. It was also found that natural recovery of these contaminated lakes is highly unlikely because the redox profile of lake sediment causes arsenic concentrations to remain highest at the water sediment interface, even if tailings are buried.

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Chapter 1: Introduction

Silver was discovered near Cobalt in 1903 by Frank LaRose as the northern Ontario railroad to the agricultural rich area of New Liskeard was being built. Not long after the initial discovery, several mines opened and alongside them several mills were constructed to crush and pre-process the ore prior to smelting, which did not take place in Cobalt. The milling process was fairly crude at first and traditional extraction methods did not work effectively on the complex ores of silver and cobalt from Cobalt (Reid et al., 1922). These tailings were often disposed of as quickly and conveniently as possible, which often resulted in directly dumping them in the nearby lakes and wetlands. Advancements in milling and refining technology allowed the tailings to be re-processed for additional profits, which meant many of the lakes had to be completely drained to obtain this material. The arsenic that was intimately associated with the ores in Cobalt, was not extracted during processing and remains in this waste. Much of this arsenic-rich waste remains in the environment today and there are obvious environmental, health, and toxicological concerns for this heavily impacted mining region. This issue also raises the question of what natural background conditions were like in this region prior to mining. Since environmental policy was non-existent when these mines operated, there is no environmental data that pre-dates mining activity. Also, with all of the mineralization in the area, evidenced by the immense amount of silver mined, the geochemical background would be substantially elevated in this region for ore related elements compared to non-mineralized adjacent areas. With this in mind, our research objectives for this thesis project were to examine the magnitude and spatial extent of arsenic contamination in

surface waters and sediment in the Cobalt region of northeastern Ontario and to determine realistic restoration targets for arsenic concentration in lake ecosystems.

To meet these objectives, in Chapter 3, I first investigated the nearby and geologically similar areas of Temagami and Gowganda using publically available lake sediment databases from the Gowganda and Temagami regions produced by the Ontario Geological Survey (Hamilton, 1997; Takats and Dyer, 2004). The primary objectives of this chapter were to investigate the natural variability in background and anomalous concentrations of arsenic (and Cobalt-type mineralization indicator elements) in relation to the bedrock geology. This study uses a space for time substitution to suggest possible restoration targets for arsenic in lake sediment in the Cobalt region.

In Chapter 4, I sampled surface waters and sediment core samples from 25 lakes (13 contaminated and 12 controls) in the Cobalt region. The objectives of this chapter were to assess the magnitude and spatial extent of arsenic contamination and to determine a realistic restoration target for these contaminated lakes that pre-dates mining activity. This was done by using control lakes from unexploited catchments and sampling lake sediments in contaminated lakes that pre-dated mining activity.

Together, this research represents some of the most extensive analyses of the magnitude and spatial extent of legacy arsenic contamination associated with the early 20th silver rush in northeastern Ontario (Dumaresq, 1993; Kelly, 2006). These data are essential to help us understand the legacy impacts and ongoing environmental degradation associated with historical mining activities. Arsenic concentrations can vary widely in nature and if restoration is to take place it is important that restoration targets are based on the best available scientific evidence for that region. These results can help

inform management and restoration plans for a region that has been heavily impacted by legacy arsenic contamination.

Figure 1.1: Map showing study areas of Cobalt, Silver Center, Gowganda and Temagami. The grey area highlights the areas sampled by the Ontario Geological Survey Lake Sediment Program

Chapter 2: Literature review

Elevated concentrations of metal contaminants in and around mining areas related to past mining, milling, and refining activities are a major environmental concern (Lottermoser et al., 1999; Marques et al., 2001). Most commonly, mine waste issues are related to acid mine drainage due to sulfide bearing minerals oxidizing to produce sulphuric acid, resulting in waters with extremely low pH. Metals are more soluble and mobile under these low pH conditions and hence drainage from these sites can be extremely toxic. The mine tailings near the Town of Cobalt, in northeastern Ontario, are somewhat unique in that they produce neutral to alkaline drainage due to an abundance of carbonates that neutralize acid producing reactions (Kelly, 2006). Metal solubility is reduced in neutral-alkaline conditions but surface waters draining away from the mining impacted areas in Cobalt still contain elevated concentrations of metals and metalloids, particularly arsenic (Dumaresq, 1993; Kelly, 2006).

The contamination of legacy mining areas can often be attributed to poor mining practices that were common place in the early days of mining. This, in conjunction with the fact that precious metals, such as gold, silver, and copper, are often associated with toxic metals and metalloids, like arsenic and mercury, which are not removed during the milling and refining process, creates waste that can be enriched in toxic metals that pose the greatest threat to environmental and human health. In the Cobalt ores, arsenic is the primary metal of environmental concern. Arsenic is leached relatively easily, is mobile in the environment, and redox sensitive, which make it a particularly troublesome metal to contain. It can easily be dispersed from its point of origin in the physical state (in the form of mine tailings) where it can become a source of contamination downstream but

also in the dissolved state where it can severely impact aquatic environments (Sprague et al., 2016). Moreover, dissolved arsenic is readily sequestered by Mn-Fe oxides, organic matter, and clays where it can become a source of arsenic that can negatively impact the chemical structure of lake sediments and biological communities that dwell in them.

From an environmental perspective arsenic is viewed negatively due to its toxicity.

However, from a geological perspective, it is often a useful indicator element that can be used in the target generation phase of mineral exploration. In Cobalt, and adjacent areas, arsenic is intimately associated with high-grade silver that is often found with cobalt, nickel, antimony and copper, hereafter, referred to as Cobalt-type mineralization.

2.1 Mining History (Cobalt, Silver Center, Gowganda and select deposits from Temagami)

The town of Cobalt is located in northeastern Ontario and was established in 1906 after the discovery of silver in 1903 during the expansion of the northern railway to the agricultural, clay-rich, lands of New Liskeard. Cobalt is famously named after the “Cobalt Bloom” (erytherite) that was often the initial point of discovery on the properties that led prospectors to identifying many of the silver deposits in the area.

Following the Cobalt silver discovery in 1903, prospectors began the search for other significant silver deposits by searching for areas where the Nipissing Diabase occurred, which was spatially and genetically associated with the silver (McIlwaine, 1978). Several smaller camps were discovered in the South Lorrain area (Silver Center) in 1907, Elk Lake in 1906, and Gowganda in 1907 (McIlwaine, 1970). The discovery of Silver Center, made 26 km southeast of Cobalt, was smaller than Cobalt but still economically important. Silver Center boasted 3 large mines, the Keeley, Frontier, and

Wettlaufer, that provided the bulk of the production for the area (McIlwaine, 1970).

Declining ore reserves and the stock market crash of 1929 resulted in plummeting silver prices in the years to come; the mines in Silver Center could not remain profitable and by 1932 the last mine, the Frontier had ceased all operations. Reports indicate that Silver Center produced more than 23,338,906 oz of silver and 3,490,377 lbs (50,901,331 oz) of cobalt by 1968 (McIlwaine, 1970).

The first discovery of silver at Gowganda was made in 1907 at Bloom Lake and by 1910 ore was being shipped from several mines in the area (McIlwaine, 1978).

Discoveries continued and by 1925 there were 14 mines producing ore, with the chief producer being the O'Brien mine on Miller Lake (Moore, 1955). By 1925 most of the mines had closed due to poor ore reserves although some of the more prosperous mines did manage to maintain operations through the economic hardships of the stock market crash and great depression. By 1969 the mines from Gowganda produced a total of 60,174,041 oz of silver and 1,325,612 lbs (19,331,842 oz) of cobalt (McIlwaine, 1978).

The mining history in the Temagami region is more diversified with the primary commodities being copper and iron with smaller deposits of gold, silver and nickel. Contamination in the Temagami area is less significant compared to Cobalt, Silver Center, and Gowganda. The most prolific deposits in the Temagami area were the Copperfields copper mine and the Sherman iron ore mine. There are several gold, nickel and Platinum Group Element occurrences that produced, but insignificant amounts to sustain operation (Simony, 1964; Bennett, 1978).

In Cobalt, after the discovery in 1903 mining activity quite literally boomed and by 1911 there were more than 40 mines operating in the area that produced 29,000,000 oz

of silver in that year alone. Mining activity in the Cobalt camp flourished until 1923 but then steadily decreased into 1930s and the last operating mine was closed in 1989 due to low silver prices (Anderson, 1993). Significantly more production came from the Cobalt camp, producing 420,550,000 oz of silver and 24,833,000 lbs (397,328,000 oz) of cobalt from 1903 to 1962 (Thomson, 1964). At today's prices for those commodities (\$24.5/oz Ag and \$17.73/lb Co in CAD) the dollar value of the production from Cobalt and Silver Center amounts to more than \$11 billion CAD. This mining was important for the early economic development of Ontario, from mining royalties and for the advancement of mining in Canada, through improvements in technology, prospecting and financial backing for future mine developments. A number of these operations had their own mills that processed the material for silver, cobalt and nickel on site. The arsenic that was intimately associated with the ore was not extracted, and remained in the silt to sand sized tailings material that would be dumped conveniently into nearby depressions, which were often wetlands and lakes. Combined, the production from Cobalt and Silver Center yielded an approximate 158,048,150 lbs (2,528,770,400 oz) of arsenic that was associated with the ore (Thomson, 1964).

Today, the town is a shadow of its former self and all that remains of the immense wealth that was generated there are the few headframes and mine workings that are a tourist attraction for the small town. Aside from obvious land-use changes on the mine properties, one of the consequences of this early mining was the vast amount of arsenic-rich waste that was produced and left to freely migrate through the environment.

2.2 Arsenic Geochemistry

The ores that occur in Cobalt are chemically complex and arsenic is intimately associated with many of the ore minerals that occur within Cobalt-type mineralization (Table 2.1). A more complete description of ore mineralogy can be found in Petruk (1971) and Boyle and Das (1971).

Table 2.1: Arsenic ore-bearing minerals occurring in Cobalt-type mineralization (from Petruk, 1971 and Boyle and Das, 1971).

Mineral Group	Mineral Name	Chemical Formula
Arsenides	Nickeline	NiAs
	Langisite	(Co,Ni)As
	Safflorite	(Co,Fe,Ni)As
	Loellingite	FeAs ₂
	Rammelsbergite	NiAs ₂
	Skutterite	(Co,Fe,Ni)As ₃
Sulfarsenides	Cobaltite	(Co,Fe,Ni)AsS
	Gerdorfite	NiAsS
	Arsenopyrite	FeAsS
	Alloclatite	(Fe,Co)AsS
Arsenates	Erytherite (Cobalt Bloom)	Co ₃ (AsO ₄) ₂ ·8H ₂ O
	Annabergite	Ni ₃ (AsO ₄) ₂ ·8H ₂ O
	Scordite	(Fe,Al)AsO ₄ ·2H ₂ O

These metals and associated arsenic can be made mobile through various oxidation reactions that are often dependent upon the prevailing redox conditions, pH, and availability of water; they are complex and not completely understood (Dumaresq, 1993). Once mobilized from their mineral state they can be found in surface waters in its oxidized form as arsenate, As(V), (AsO₄)³⁻, in its reduced form arsenite, As(III), (AsO₃)³⁻, or in its organic form as methylated As(V) compounds (Cullen and Reimer, 1989; Percival et al., 2004). Arsenic is mobile both in acidic, neutral and alkaline waters due to its amphoteric nature. The oxidized form, As(V), is more common than the reduced form and is more typical of surface waters due to the aerobic conditions found there. Reduced

arsenic, As(III), is less common in surface waters, and is more prevalent in groundwaters where anoxic or strongly anaerobic conditions that create reducing conditions are present (Casiot et al., 2007). Percival et al. (2004) found that As(III) represented approximately only 13% of total arsenic species in a wetland survey conducted in Cobalt. Bacteria can use arsenic as a source of energy by reducing As(V) to As(III) in anaerobic conditions with organic matter acting as an electron donor, conversely in oxidizing conditions, As(III) can be oxidized by bacteria to As(V) using nitrate or oxygen as an electron acceptor (Lloyd et al., 2006). As(V) is chemically more stable because it is more easily sequestered than its reduced counterpart (Gaskova et al., 2003; Casiot et al., 2007; Paktunc, 2013), and approximately 60 times less toxic (Kreidic et al., 2011). In the terrestrial environment, the near surface zone of tailings deposits is identified as the main area for arsenic mobilization (Gaskova et al., 2003; Kwong et al., 2006; Lim et al., 2009; Foli et al., 2012; Paktunc, 2013). In Cobalt, the upper levels of these tailings deposits also display enriched metal concentrations and metalliferous crusts can be found on their surfaces that can contain up to 200% more arsenic compared deeper tailings (Dumaresq, 1993; Sprague et al., 2016). This zone of tailings is most subject to rapid changes in redox conditions, due to such events as rainfall, freezing, thawing, fluctuations in the water table and evaporation in addition to being more susceptible to erosion, all of which promote mobilization and further dispersal into the environment.

Arsenic is known to have harmful effects on human health; even at low concentrations prolonged exposure can negatively impact human life (Health Canada, 2006). Acute (days to weeks) arsenic exposure at concentrations greater than 10 µg/L (Canadian drinking water standard) can result in abdominal pain, vomiting, diarrhea,

numbness in hands and feet, and temporary loss of movement and sensory responses (Health Canada, 2006). Long term (many years to decades) arsenic exposure have been shown to be unequivocally carcinogenic for humans that can manifest itself as skin cancer (Begerow et al., 2012) or in internal organs such as the bladder, liver, and lungs (Health Canada). Lower blood production in the form of anemia, numbness in the hands and feet, and abnormal heart rhythms are also symptoms of long term exposure to arsenic. The inorganic forms of arsenic can only been absorbed by humans after ingestion and are not absorbed through the skin (Health Canada, 2006). Inorganic arsenic is also more toxic than the methylated forms (Begerow et al., 2012).

2.3 Lake Sediment and Arsenic

The physical, biological, and chemical structure, and the rate of accumulation of lake sediments are influenced both directly and indirectly by the physiography of the watershed and climate of where the lake is situated (Takats and Dyer, 2004; Brothers et al., 2008). Lake sediments act as integrators of watershed wide environmental information including the bedrock geology, glacial till, vegetation, and hydrology of the watershed (Wei and Wen, 2012; Alfonso et al., 2015; Couillard et al., 2004, 2008; Takats and Dyer, 2004). The elements found in lake sediments may be in several forms and include the constituents of primary rock forming minerals, secondary precipitated minerals formed through weathering, minerals typical of mineralization, ions adsorbed to clays and Fe-Mn oxides and absorbed into organic matter (Rose, 1975). By sampling lake sediments, a single sample can represent an extremely large area (Smol, 2008) and by sampling a large number of lakes within a region, a great deal of information can be extracted to gain an understanding of regional and local background conditions (Soranno et al., 2010).

Lakes are typically oxidizing in surface waters and directly at the water-sediment interface (WSI) and are reducing below this zone (Couture et al., 2010). This redox profile significantly impacts the chemical structure of lake sediments, particularly due to Mn-Fe oxides that have unique adsorption properties making them effective metal scavengers under oxidizing conditions (Couture et al., 2010). However, once buried by new sediment these Mn-Fe oxides encounter reducing conditions and undergo reductive dissolution, releasing their previously scavenged metals. This process, coupled with the fact that arsenic is also redox sensitive and more mobile under reducing conditions, creates a continual redox cycle that maintains the highest concentrations of metals in the surface sediments. In contaminated systems, such as in Cobalt, this process is increased dramatically, because buried tailings and surface waters both act as sources of metals, and can result in surficial sediments having arsenic concentrations that exceed their source material. Arsenic can also move in the down core direction if proper conditions are met, such as hydraulic or chemical gradients (Nikolaidis et al., 2004; Andrade et al., 2010). This cycle also complicates the determination of background conditions because there is a continual movement of elements toward the water sediment interface, but also potentially down core. The process of remobilization during burial is not a complete one, therefore the sampling deeper sediments (>20 cm) can yield a reliable sample that can resemble background levels (Takats and Dyer, 2004).

Lake sediments also support a vast benthic ecosystem that is tightly coupled to the open water environment of lakes (Vadeboncoeur et al., 2002). One can easily imagine how the aforementioned redox cycle could impact the benthic community that primarily dwell in the upper sediment (Bettinetti et al., 2012). In an effort to protect aquatic

ecosystems, Canada has set objectives for metal concentrations in sediment for the protection of aquatic life (CCME, 2001). Results in this document are often compared to these objects for toxicological context.

2.4 Previous Work in Cobalt

Previous work in the Cobalt region have highlighted that the tailings are actively migrating through the environment and releasing significant amount of metals to the surface waters (Sprague et al., 2016). Although this particular study indicated that no statistically significant differences existed between the source tailings and migrated tailings downstream, both sites contained arsenic that greatly exceeded background and regulatory objectives. Also, given that the migration has been occurring over a long period of time this could simply indicate that metals are being released at relatively equal rates regardless if they are located at the source or not. The study also showed that waste rock is a significant contributor to elevated metal concentrations in surface waters (Sprague et al., 2016). The most extensive environmental study in the Cobalt region was done in the early 1990s by Dumaresq (1993). He focused on tailings geochemistry and surface water interactions and conducted the majority of groundwork for the area, characterizing the tailings from a geochemical perspective. Dumaresq (1993) estimated that as much as 18,000 kg (+/- 9,000 kg) of arsenic were being released annually from tailings sites in the Cobalt area to Lake Temiskaming, the headwater for the Ottawa River. Dumaresq (1993) also showed that the tailings are chemically complex and undergoing chemical evolution through processes like supergene that promoted the release of metals. These processes are enhanced by the fact that the tailings have little to no remedial work done on them, and remain susceptible to the forces of nature.

Beauchemin and Kwong (2006) conducted leaching experiments to demonstrate that arsenic is rapidly mobilized with rapid redox changes, even under alkaline conditions found at Cobalt. They also postulated that arsenic release may be microbially mediated. Kwong et al. (2007) investigated the arsenic rich mine waste and concluded that submerged tailings are likely a source of arsenic to surface waters rather than a sink. They also showed that Al-bearing minerals can act as a major sorbent in the region (Kwong et al., 2007). Kelly (2006) investigated the large tailings deposit at Crosswise Lake and the downstream wetlands in the Farr Creek drainage basin from a biogeochemical perspective. In contrast to Kwong et al. (2007) findings, Kelly (2006) concluded that the wetland in the drainage basin acted as a sink of metals rather than a source, with roughly 75% of the metals being retained in the sediment and the remaining 25% being taken up by cattails, *Typha latifolia*. Arsenic, in particular, was found to be most associated with the residual and organic fractions of sediment. Kelly's study highlighted that redox conditions were localized and that under oxidizing conditions arsenic was likely to be sequestered by prevalent Fe-Mn oxides, and under reducing conditions, sulfides and organic matter were effective attenuators (Kelly, 2006). Kelly also noted the importance of this system being alkaline and attributed much of the attenuation ability of the wetland to this effect (Kelly, 2006).

More recent studies in the area (Hyden et al., 2016) have investigated the impacts of tailings migration in lake ecosystems from a biogeochemical perspective, using diatoms species assemblages to assess conditions prior to, during, and after the first appearance of tailings. Results of the study indicated that the first appearance of the tailings in the lake significantly altered the species assemblages having an overall

negative impact the lake ecosystem. Hyden et al. (2016) also concluded that biological recovery of the system was highly unlikely without external remedial assistance because concentrations of arsenic at the water sediment interface are enriched from contaminated surface waters and tailings below the water sediment interface.

In many ways, the environmental issues surrounding the Cobalt, Ontario, area parallel the issues surrounding the Giant Mine near Yellowknife, Northwest Territories. However, Cobalt has received much less media and scientific attention. The primary element of concern for both locations is arsenic and the environmental issues are similar; widespread contamination of arsenic rich mine waste in surface waters and submerged lacustrine sediments. Concentrations of arsenic in surface waters and tailings are similar to those found in the Cobalt mining area, with arsenic in pore waters and sediment in Yellowknife Bay reaching 585 µg/L and 1310 mg/kg, respectively (Andrade et al., 2010). In many cases, arsenic concentrations in the Cobalt area greatly exceed those found in the areas impacted by the Giant Mine (Houben et al., 2016). The impacted area also affects roughly the same immediate population, and arguably more, as drainage from Cobalt flows into Lake Temiskaming, the headwater of the Ottawa River. One could easily argue that the environmental issues in Cobalt, ON, deserves equal attention to those of Giant Mine and that restoration and remediation efforts are warranted in the Cobalt region to mitigate some of the environmental harm from legacy arsenic contamination.

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Chapter 3:

The landscape-scale relationship between lake sediment geochemistry and catchment bedrock composition from important precious metal mining regions (Temagami and Gowganda areas) of Northeastern Ontario, Canada

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This chapter will submitted to a peer reviewed journal

Author contributions: DDS developed the project idea, DDS and JCV analyzed the data, DDS and JCV wrote the manuscript.

Abstract

Lake sediments are integrators of watershed wide environmental information that includes bedrock geology, glacial overburden, vegetation, hydrology and land-use. Lake sediments were collected from an area covering approximately 13,600 km² from the Gowganda and Temagami regions to determine the geochemical background conditions representing different bedrock types. Catchments with Nipissing Diabase had the highest background levels for arsenic (10 mg/kg). The major geological controls influencing changes in lake sediment geochemistry were also determined using random forest classification and principal component analysis (PCA). Random forest classification was able to identify which geological province the samples were derived from and the dominant rock types in the samples catchment with respectable accuracy. PCA revealed strong spatial relationships between lake sediment geochemistry and bedrock geology highlighting several important features. The PCA showed a strong spatial relationship between Nipissing Diabase and the Cobalt-type mineralization indicator elements. This study demonstrates that unique geochemical assemblages can be associated with specific geological areas which is of interest to exploration geologists, for target generation and prospecting, and to environmental policy makers, for site specific restoration targets.

3.1 Introduction

The physical, biological, and chemical structure, and the rate of accumulation of lake sediments are influenced both directly and indirectly by the physiography of the watershed and climate of where the lake is situated (Takats and Dyer, 2004, Brothers et al., 2008). In this way, lake sediments form a valuable record of historical environmental change, including land-use and climate change (Smol, 2008). Lake sediments are also integrators of watershed wide environmental information including the bedrock geology, glacial till, vegetation, and hydrology of the watershed (Wei and Wen, 2012; Alfonso et al., 2015; Couillard et al., 2004, 2008; Takats and Dyer, 2004). The elements found in lake sediments are related to the rocks and soils that they were weathered from (Rose, 1975) and therefore lakes, particularly those formed through glacial erosion (Panahi et al., 2004), serve as effective traps for these surficial elements as they accumulate coarse and fine sediments from their watershed.

The elements found in lake sediments may be in several forms and include the constituents of primary rock forming minerals, secondary precipitated minerals formed through weathering, minerals typical of mineralization, ions adsorbed to clays and Fe-Mn oxides, and ions absorbed into organic matter, which can make up a large component of lake sediments (Rose, 1975). As a result, lake sediments are integrators of watershed structure and processes by which a single sample can represent an extremely large area (Smol, 2008) and, by sampling a large number of lakes within a region, a great deal of information can be extracted to gain an understanding of landscape-scale environmental conditions (Soranno et al., 2010). Due to their role as integrators of watershed processes lake sediments offer the potential as a tool for rapid mineral exploration (Cameron, 1977;

Cameron, 1978; Panahi et al., 2004) and as sentinels of environmental change occurring in the watershed such as pollution (Andrade et al., 2010; Parviainen et al., 2012), climate change (Kaufman, 2009; Garçon et al., 2012;), and land-use change (Vermaire et al., 2011).

Lake sediments also support a vast benthic ecosystem that is tightly coupled to the open water environment of lakes (Vadeboncoeur et al., 2002). In an effort to protect aquatic ecosystems Canada has set objectives for metal concentrations in sediment for the protection of aquatic life (CCME, 2001). In order to better understand the complex relationships between watershed physiography and metal concentration in lake sediments a landscape approach offers the potential to classify lakes based on background metal concentration in lake sediments (Sorranno et al., 2010). These landscape-scale lake classifications can help us better understand natural variation in metal concentrations in lake sediment and help us tease apart anomalously high readings as either naturally occurring due to mineralization within the catchment or anthropogenic due to pollution.

In Canada, the Ontario Geological Survey (OGS) has been particularly active in collecting massive datasets of lake sediment geochemistry and have published vast amounts of geochemical data that covers large areas within Ontario. In this study, two OGS lake sediment geochemistry datasets are used from the Gowganda and Temagami areas in Northeastern Ontario to examine background and anomalous geochemical signatures within these areas. These study regions have important precious metal exploration and mining histories in Canada but also have highly contaminated sites due to legacy mining activities (Sprague et al., 2016). Therefore, these study regions offer the potential to examine natural variation in lake sediment geochemistry in an area rich in

mineralization in addition to providing a landscape-scale approach to quantifying background sediment geochemistry for restoration of legacy contamination sites. The two sampling areas span geologically similar terrain, with the majority of samples (76%; n=2750) located in the Archean Superior and Proterozoic Southern provinces, and the remaining 24% (n=853) coming from the Grenville geologic province. These two locations were selected because they share similar bedrock characteristics with the Cobalt mining camp, which is an area heavily impacted by high sediment arsenic concentrations (up to 1600 times higher than environmental guidelines) due in-part to legacy mine contamination (Dumaresq, 1993; Sprague et al., 2016).

The objectives of this study are to investigate the natural variation of elements in lake sediment in a heavily mineralized study region to establish background and anomalous concentrations in various regionally common geologic terrains and to assess the link between lake sediment geochemistry and the composition of the bedrock geology of the lakes catchment. These results will help improve our understanding of natural variability in lake sediment metal concentrations in heavily mineralized regions, where most hard-rock mining occurs and where most hard rock mining-related environmental restoration work is required. Furthermore, these data are valuable for establishing realistic restoration targets for legacy contamination sites such as Cobalt, Ontario, where no environmental baseline data was collected before the mining operation.

3.1.2 Study Region

The study areas are located in northeastern Ontario, centered on the Gowganda and Temagami areas. These study areas were chosen because they are in close physical proximity to each other and share many characteristics, including boreal forest

vegetation, glacial overburden, bedrock geology, and rare mineralization processes, particularly the Cobalt-type (Ag-Co-Ni-Sb), mineralization style (Bennett, 1978; McIlwaine, 1978; Hamilton, 1997; Takats and Dyer, 2004). The study areas encompass a total surficial area of 13 500 km² (Figure 3.1) and contains thousands of lakes.

3.1.3 Bedrock Geology

Both the Gowganda and Temagami areas have prolific mining histories highlighting several mineralization styles. Gowganda is renowned for its Cobalt-type mineralization and several smaller gold deposits (McIlwaine, 1978; Andrews et al., 1986; Fyon et al., 1992; Hamilton, 1997) whereas Temagami has a more diversified mining history with copper, silver, gold and iron being the primary commodities from several mines (Grant, 1964; Bennett, 1978; Takats and Dyer, 2004). The bedrock geology in the southern and superior provinces of the Temagami-Gowganda areas are quite similar in distribution and composition (Figure 3.3.1). They are mostly overlain by sedimentary rocks of the Huronian Supergroup, namely the Lorrain and Gowganda formations.

The Lorrain formation conformably overlies the Gowganda and is generally a feldspathic arkose to quartz arenite with beds of polymictic pebble conglomerate (McIlwaine, 1978; Bennett et al., 1991). The Gowganda formation unconformably overlies the Archean basement rocks. It is classified by two members, the Firstbrook and Coleman. The Firstbrook member is a reddish laminated argillite while the Coleman member can be characterized by conglomerate, greywacke and argillite layers (Bennett et al., 1991; Takats and Dyer, 2004). Supracrustal Archean basement rocks are composed of intercalated felsic to mafic metavolcanics flows (Keewatin) with minor ultramafic components (Bennett et al., 1991; Hamilton, 1997). Intrusive felsic (Algonian Granites)

rocks make up roughly the same areal extent (Hamilton, 1997). Intruding into all of these rocks is the Nipissing diabase, which is a large mafic sill that is semi-continuous throughout the study areas (Bennett et al., 1991; Takats and Dyer, 2004). The intrusion of the Nipissing Diabase, a quartz gabbro 2.2 Ga in age, is considered to be the most significant geologic event for the area as many mineral deposits are spatially related to it, namely the Ag-Co deposits of Cobalt, South Lorrain and Gowganda, hereafter referred to as Cobalt-type (McIlwaine, 1978; Takats and Dyer, 2004).

The Grenville province, south of Temagami, is considerably different as it is a complex orogenic belt about 1 Ga in age. Its mineral potential is considerably lower than the other areas examined and has no prolific mining camps or mineral deposits associated with it.

3.1.4 Metamorphism and Structural Geology

The structural geology of the study areas can be complex on a local scale but on a regional scale can be summarized into a few important events. Generally speaking, faults and fractures of the Temagami and Gowganda regions act as significant controls on mineralization, especially north trending faults that occurred in the Archean and were reactivated during the intrusion of the Nipissing Diabase (Bennett, 1978; McIlwaine, 1978; Andrews et al., 1986). Metamorphism throughout the southern and superior geological provinces is generally low and within low greenschist facies (Bennett et al., 1991), although shear zones may exhibit higher grades. Metamorphism in the Grenville geologic province is considerably higher in upper amphibolite facies and can be up to the granulite facies (Takats and Dyer, 2004). A zone of intense deformation, folding and

faulting exists for several kilometers perpendicular to the contact zone between the two geologic provinces, known as the Grenville front tectonic zone (GFTZ) (Easton, 1992).

3.1.5 Glacial till

Overburden throughout the majority of the study region is a thin bedrock drift complex (Barnett et al., 1991) with smaller occurrences of glacial till, eskers, glaciofluvial outwash, and glaciolacustrine deposits (Takats and Dyer, 2004). Glacial striations indicate 3 dominant glacial directions, beginning with a southwesterly, then southerly and finally southeasterly movements (Takats and Dyer, 2004). There is little reported difference in the make-up of the glacial till throughout the study region (Barnett et al., 1991; Takats and Dyer, 2004).

3.2 Methods

3.2.1 Sampling, Sample Preparation, Geochemical Analysis and Pre-Screening

Sediment samples were collected and analyzed by the OGS as part of their surficial geochemistry program. A full description of the OGS sampling, analyses, and quality control protocols can be found in Hamilton (1997) and Takats and Dyer (2004). Samples were collected from the Gowganda silver region by the OGS in the summer of 1996. A total of 1172 lake sediment samples were collected from an area covering 2700 km². In the summers of 2002 and 2003 another lake sediment project was undertaken by the OGS in the nearby Temagami area (Figures 1). From the Temagami survey 2441 lake sediment samples were collected from an area covering 8900 km². In both projects samples were collected using a gravity corer to retrieve a stratified sediment core from the center of the lakes at maximum depth (z-max). Samples taken from max depth are

desirable because due to sediment focusing these sediments best represent a whole lake signal. Samples were taken at a core depth of 20 cm below the water-sediment interface to reduce the influence of Mn-Fe metal scavenging, redox cycling of elements and in an attempt to sample sediments accumulated before the onset of major industrial activity (Hamilton, 1997; Takats and Dyer, 2004).

In preparation for metal analysis, sediment samples from each lake were dried at 40°C, crushed and sieved to obtain -80 mesh (<177 µm) size fraction and homogenized (Takats and Dyer, 2004). Loss on ignition (LOI) was conducted as a measure of organic content. Chemical analysis of these samples was undertaken at the Geolabs laboratory at the OGS in Sudbury, Ontario. Approximately 0.5g of the homogenized sample was digested in an aqua regia solution (3:1 molar ratio of HCl to HNO₃) and analyzed using both Induced Couple Plasma – Mass Spectrometry (ICP-MS) and ICP – Optical Emission Spectrometry (ICP-OES) to determine approximately 50 trace elements. Ten grams of sample were used for induced neutron activation analysis (INAA) for gold and arsenic and a suite of platinum group elements. Quality assurance and control was stressed with 1 in 10 samples being a control to evaluate lab and contractor performance.

The OGS lake sediment geochemistry data were obtained from publicly available data on the geology Ontario website (geologyontario.mndmf.gov.on.ca). Supplementary data, bedrock and geophysical maps and reports, were also obtained from this website. Because the goal of this study was to understand natural variations in lake sediment geochemistry an initial screening of the data was carried out to remove samples that were clearly influenced by past mining activity, (i.e. the lake sediment samples displayed extremely high levels of metals and the lakes were located near known historical mining

activity). This initial screening activity removed 17 locations (0.5%) lakes from the initial dataset.

3.2.2 Statistical Analyses

In exploration and environmental geochemistry, background concentrations of sediment geochemistry are often calculated by taking the range of data that falls within ± 2 standard deviations of the mean (Reimann et al., 2005; Teng et al., 2009). This approach typically results in 95% of the data representing background concentrations and the remaining 5% being attributed to anomalous outliers (Reimann et al., 2005). One drawback of this classical approach is the strong influence that these outliers have on the calculation of the mean and standard deviation, which could potentially skew estimates of background geochemistry (Reimann et al., 2005). Cumulative frequency curves (CF-curves) reduce the potential effect of these outliers on the calculation of background geochemistry and are used in this study because they display the entire data distribution and the inflection points of the curve provides a flexible and reasonable separation between outliers and background variation (Reimann et al., 2005; Matchullat et al., 2009; Wei and Wen, 2012). The natural variation in background geochemistry concentrations can be seen as the linear portion of the CF-curve for a particular element. The upper limit of the background variation in the CF-curve is termed the environmental threshold and can be seen as the inflection point on the CF-curve. The environmental threshold typically contains 85-95% of the data and represents the boundary between anomalous and background values (Teng et al., 2009). Concentrations are considered to be anomalous if they are above the environmental threshold on the cumulative frequency curve (Wei and Wen, 2012).

The CF-curves were used to establish background concentrations for 5 elements (Ag, As, Co, Sb, Ni) selected based on their relationship to Cobalt-type mineralization for the entire dataset as well as subsets of data based on the rock types within catchment basins. This was done as a preliminary test to examine if large differences existed in the background concentrations between the two study areas, (i.e. Superior and Grenville geologic provinces) and specifically to test if catchment basin lithology could be a dominant factor in the metal concentrations observed. To test the relationship between metal concentrations and lithology the CF-curves were created using sediment samples that strongly represented each lithology. This typically meant selecting lakes where ~75-100% of the catchment area was occupied by the representative lithology. To examine how the landscape-scale distribution of sediment geochemistry compares to regulatory standards the distributions of metals as represented by the CF-curves were compared to the Ontarian and Canadian guidelines for the protection of human and aquatic life.

A random forest approach was first used to test if lake sediment geochemistry could be distinguished based on which geologic region they were located. RF was then used to test if sediment geochemistry could be distinguished based on the dominant rock type in their catchment basin. Random forest is an ensemble classification method developed by Breiman (2001). It is a popular classification method because classical classification methods are highly sensitive to the input data and small modifications in the settings or data can produce different results (Baudron et al., 2013). Ensemble learning models like random forest are often used because the randomization procedure used in the classification trees and subsequent voting system reduces the sensitivity to minor changes in input data that would greatly impact classic classification models.

In random forest, a large number of independent classification trees were generated based on bootstrap re-sampling of the dataset 999 times. For the bootstrapping procedure, each tree was created by randomly partitioning the dataset into training data (in bag), which represents 2/3 of the data and validation data (out of bag) which represents the remaining 1/3 of samples. The classification trees were then created using a randomized subset of the variables (equal to the square root of total variables) as predictors of the bootstrapped data (Harris and Grunksy, 2015). For example, in our study 54 elements from the lake sediments were used in total, therefore for each tree 7 randomly selected elements were used as predictors. At each node within a classification tree the best split is based on the Gini index. The Gini index is a measure of homogeneity and works by selecting the set of variables and numerical threshold that maximizes homogeneity within each node and heterogeneity between nodes (Cracknell and Reading, 2013). Trees continue to grow until splitting can produce no further reduction in the Gini index (Baudron et al., 2013; Cutler et al., 2007). This process effectively reduces correlation and adds an element of randomization to the classification trees.

Once all the trees are created through the randomization process a majority vote system using the out of bag classifications is used to assign a class to each sample. With each sample having been included in the out of bag observations for several trees its class has been estimated several times and the majority class that was assigned becomes the final classification. The majority vote system works by assigning each sample with the class that was assigned to it the most often. Random forest also shows how many times samples were improperly classified, and to which class it was improperly assigned to and which variables were the most important in determining accurate predictions. This is

important because it highlights which elements are influential for distinguishing each region or rock type from one another. Random forest was conducted using the RandomForest package (Liaw and Wiener, 2015) in the R statistical language software (R Core Team, 2015).

Principal component analysis (PCA) was used to examine the dominant trends in the lakes sediment geochemistry data (Reid and Spencer, 2009). PCA is frequently applied in multivariate environmental data such soils (e.g. Zhang, 2006; Sadeghi et al., 2014), surface and groundwater (e.g. Zaharescu et al., 2009; Monjerezi et al., 2011), sediments (e.g. Bellehumeur et al., 1993; Panahi et al., 2004), contaminants (e.g. Borvůka et al., 2005; Sprague et al., 2016; Zhang, 2006), biological communities (e.g. Vermaire et al. 2011; Upiter et al. 2014) where numerous variables have complex inter-relationships. In large datasets, the variance amongst samples is often too great to be explained by traditional linear models and classification approaches, therefore PCA is a well-established technique that reduce the dimensions of the dataset to allow for meaningful interpretations (Reid and Spencer, 2009).

Before the PCA was conducted the geochemical data were center log-ratio (clr) transformed to correct for closure and non-normally distributed data. The clr transformation is achieved by dividing each variable by the geometric mean of the composition of the individual observations and then taking the logarithm (Aitchison, 1986; Grunksy et al., 2014). The PCA was conducted on the Gowganda and Temagami areas separately as an initial PCA run with the datasets combined determined that the first principal component was simply separating the two study regions, overshadowing variances within each dataset that is of interest. PCA sample loadings were extracted

from each dataset to support interpretation using a sample loading values of greater than 0.1 or less than -0.1. To examine spatial relationships and the distribution of variance determined by the PCA component scores were mapped using ArcGIS (10.3.) and interpolated using empirical bayesian kriging methods. The number of significant components to retain from the principal component analysis was determined following the broken stick criterion (Jackson, 1993). The number of components to retain is determined at the point where the broken stick model intersects the scree plot (Phillips and Desloges, 2014). The PCA was conducted using the stats package, the data transformations were completed using the robCompositions package (Templ et al., 2011), and the broken stick model was completed using the vegan package (Oksanen et al., 2015) in R (R Core Team, 2015).

A correlation matrix was used to further investigate the relationships between environmental variables and the principal component (axes 1 through 5) scores. The environmental variables used in the correlation matrix included water quality parameters (pH, conductivity, colour of organic content), lake depth, ratio of lake area to catchment area, and the percentage of rock type within each samples catchment were analyzed. The correlation matrix was carried out using R (R Core Team, 2015).

The maps used for spatial analysis of the PCA were created using kriging methods. Kriging is a geostatistical method that employs variation, magnitude and spatial scale from samples surrounding unknown points to determine an interpolated value in unsampled locations (Chilès and Delfiner 1999; Carranza, 2009). Empirical bayesian kriging is similar to traditional kriging methods except that empirical bayesian kriging can fit several semi-variogram models to a dataset (ESRI, 2015; Pilz and Spöck 2007).

This allows for the data to be partitioned into sub-regions that have overlying trends (Mirzaei and Sakizadeh, 2016). This technique allows for the detection and representation of regions with spatial trends, cyclicity, and importantly, can highlight zones with anomalous data. Empirical bayesian kriging was carried out using the geostatistical wizard in the spatial analyst toolset in ArcGIS software (version 10.3.1).

3.3 Results

3.3.1 Geochemical Background Conditions

Background metal concentrations were determined for each rock type within the Gowganda and Temagami study areas based on CF-curves (Table 3.1). In Ontario and Canada there are regulatory values in place to protect human and aquatic life. In Ontario, the provincial regulatory concentration for arsenic in sediment within 30 meters of a water body is 6 mg/kg (OME, 2011) whereas the Canadian sediment quality guideline for the protection of aquatic life is 17 mg/kg (CCME, 1999). For arsenic, 15.7% and 2.8% of all samples in the Temagami and Gowganda data sheets exceeded the Ontario and Canadian guidelines, respectively, suggesting that the national Canadian guideline is more representative of natural arsenic concentrations in lake sediment. Within the samples that exceeded regulatory standards, over half the samples that exceeded the regulatory objectives were located in watersheds that contained Nipissing Diabase. The median values for arsenic (2.6 mg/kg) within the entire dataset were well within the prescribed limits indicating that the Canadian national objective for arsenic in sediments for the protection of aquatic life is a conservative estimate and in most cases (~97%) is obtainable in natural systems located on the Canadian Shield.

Overall, among watersheds with different lithologies the background geochemical ranges did not deviate substantially from each other, although there were some notable differences in background concentrations, particularly in catchments that favour the Cobalt-type mineralization (rock types 23d/21) with the indicator elements (Co, Ni, As, Sb). Watersheds with indications of the Cobalt-type mineralization were among the highest background ranges for the entire study area (Table 3.1). Arsenic and cobalt were also typically enriched (up to 10 mg/kg for As and up to 12.5 mg/kg for Co) in Nipissing diabase (23d) and Gowganda (21d) catchments compared to other rock types. Granitic catchments typically displayed very low levels of cobalt-type indicator elements with the exception of cobalt, however, when in contact with Nipissing Diabase (+/-Gowganda formation) metal concentrations increased (Table 3.1). Similarly, the Lorrain formation also displayed some of the lower median concentrations and lowest background ranges for most of the metals for all of the rock types, unless the Lorrain formation was in contact with the Nipissing diabase, in which case greater metal concentrations were observed (Table 3.1). Arsenic and antimony concentrations from the Superior/Southern provinces were substantially greater than those found in Grenville catchments (Table 3.1).

The CF-curves also showed the anomalous range as the second linear segment in the graphs. Similar trends between the background ranges and different rock types were observed for the anomalous ranges. Watersheds that contained predominantly Nipissing Diabase had higher values of nearly all metals in the sediment samples (Table 3.1) and a greater number of anomalous samples, including the maximum values of all rock types.

For example, the anomalous range of arsenic for Nipissing Diabase ranged between 10 and 30 mg/kg (Figure 3.3.2).

3.3.2 Random Forest Classifier

The random forest classifier was used to provide insights into the relationship between metal assemblages and catchment basin lithologies. The random forest classifier was able to accurately distinguish geological provinces with a 98% success rate for the Superior/Southern province and an 81.2% success rate for the Grenville province (Table 3.2). The out of bag error estimate for this test was 6.26%, suggesting a high predictive power of the geological province based on sediment geochemistry. Of the misclassified samples, most were located in the Grenville front tectonic zone, a transitional fault zone between the two geologic provinces. When the random forest classifier was used to classify rock types based on the lake sediment geochemistry the results were less impressive (Table 3.3). There were a large number of misclassified samples that resulted in the out of bag error estimate for predicting rock types being 35.99%. High class error for rock types 4, 5, 6, 7, 12, 39, 42 may be related to underrepresented lithologies in the dataset. Misclassifications also occurred frequently among samples originating from watersheds containing the Granite (rock type 15), Gowganda (rock type 21d), Lorrain (rock type 21c) and Nipissing Diabase (rock type 23d).

3.3.3 Principal Component Analysis and Geochemical Assemblages

Examination of the scree plots using the broken stick model suggested that the first four principal components for the Temagami PCA and the first five principal components for the Gowganda PCA were statistically significant. In our results we focus

only on principal components that are related to the research question (those that appear to have spatial relationships toward bedrock geology).

3.3.3.1 Temagami Dataset

Principal component 1 explained 30.75% of the variance of the lake sediment geochemistry and was positively related to rare earth elements and a positive spatial associations with sedimentary rocks of the southern province (Figure 3.3.3a). Principal component 2 (Figure 3.3b) explained 15.45% of the variance and largely separated the Southern and Superior provinces from the Grenville province (Figure 3.1). Component 2 had a negative relationship with the southern and Superior geologic provinces while having a positive relationship with metamorphic rocks in the Grenville province. The loadings from these components (Table 3.4) suggest that lithophile and siderophile elements are the most important variables distinguishing the Grenville province from the Superior and Southern provinces to the North. Conversely, chalcophile elements, particularly copper, sulphur, arsenic, antimony, and cadmium, were important for distinguishing the Superior and Southern provinces from the Grenville; these results are in agreement with the variable importance findings from the random forest classification.

Principal component 3 explained 10.19% of the variance and (Figure 3.3c) was spatially related to areas possessing favourable geologic conditions for Cobalt-type mineralization and anomalously high concentrations of metals; in these areas the Nipissing Diabase was in contact with the Gowganda formation, but also had a positive relationship to some areas where Archean intercalated felsic and mafic rock types were found. Component 3 was also spatially related to metasedimentary rocks in the Grenville province, this area contained elevated background concentrations of Ag, Co, Cr and As.

Notably the As, Sb, Co, Cu, Fe and Mn variables were important for delineating these regions (Figure 3.1). This relationship between principal component 3 scores was supported by these zones containing known Mineral Deposit Index points; these Mineral Deposit Index points correspond to past producing mines, prospects and mineral occurrences.

Component 5 (Figure 3.3d), was also spatially related to areas highlighted by PC3 and had similar elements showing positive loadings, in addition to Ag and Ni. Although explaining less variance (only 3.5%), and excluded by the broken stick model, the resulting areas are highly related to the Nipissing Diabase, suggesting sites consistent with the Cobalt-type mineralization. Additionally, while component 3 had a positive relationship toward Fe and Mn, which may indicate that some areas highlighted by positive component 3 scores may be more related to metal scavenging, component 5 has a negative relationship toward Fe and Mn suggesting that the positive loadings were not explained by adsorption onto Fe-Mn oxides but instead may represent mineralization within the watershed.

The correlation matrix of the Temagami data (rock types, water quality, lake properties, and principal component scores) revealed that principal component 2 is slightly ($r = 0.1$ to 0.3 ; $p < 0.05$) correlated with the ratio of lake area to watershed area and the depth of the lake. Principal component 3 was also correlated to these parameters but also showed a strong positive correlation ($r = 0.7$, $p < 0.001$) with pH. The correlation matrix did not show any statistically significant relationships for principal component 1 and principal component 5 among any of the environmental variables, suggesting that other environmental variables may be important in controlling these components.

3.3.3.2 Gowganda Dataset

In the Gowganda study area the PCA highlighted different processes and areas compared to the Temagami region. Principal component 1 (Figure 3.4a), explained 30.45% of the variance and was spatially related to the intercalated Archean volcanics in the central western portion of the study area, the silver mining area near the town of Gowganda, and zones of elevated concentrations of metals representing the positive loadings for component 1 (Table 3.5). The western area highlighted by component 1 had several gold, silver, zinc and cobalt deposits associated with it (Ayer et al., 2003) and this component could be highlighting potential mineralization in that area. The elevated component 1 scores around the Gowganda silver area are likely related to the mineralization in that area. The large area south of Gowganda centered on Beauty Lake appears to be related to the Nipissing sills in that area; in addition to the bedrock maps, gravity and magnetic maps indicate that a third diabase sill exists between the two outcropping diabase sills on the extremities of this anomalous area and extends for several km below surface in a northwesterly trend (OGS 2004; 2009a; 2009b). It is plausible that component 1 is highlighting possible mineralization in the region as there are several deposits on the extremities of the area.

Principal component 2 (Figure 3.4b) explained 13.66% of the variance and highlighted processes that are related to areas of elevated background concentration due to conditions favourable for Cobalt-type mineralization. These areas included the Archean volcanics to the west, the Gowganda silver area and contact zones between the Nipissing Diabase and Huronian Supergroup. These zones highlighted by these positive component 2 scores corresponded to positive component 2 loadings that include LOI, As,

Zn, Sb, Mo, Hg, Cu and Ag (Table 3.4). These positive loadings are similar to those in the Temagami region (component 3) that represent areas with similar geological properties. Furthermore, the contact zones highlighted by this component fit the deposit model for the area, which is similar to the Cobalt-type mineralization. The areas represented by component 2 also contained the majority of the Mineral Deposit Index points, which further suggests that this component is related to mineralization in the catchment.

The correlation matrix of the Gowganda data (rock types, water quality, lake properties, and component scores) revealed that principal component 1 was correlated to (0.2 to 0.6; $p < 0.05$) conductivity, pH, and Archean aged rock types (rock types 5, 6, 7) whereas principal component 2 was negatively correlated (-0.2 to -0.4, $p < 0.05$) with the ratio of lake area to catchment area and the depth of the lake, suggesting a possible link to a dilution of the mineralization signal with larger and deeper lakes.

3.4. Discussion

This study has demonstrated that natural variation in the background concentrations of lake sediments is related to bedrock types within their watersheds. Furthermore, distinctly different groups of lake sediments, representing both local and regional geochemical assemblages, are identified and positively related to geological processes and terrains with different properties. These results were supported by the examination of elemental distributions in samples representing different geological provinces and rock types that highlighted variance in geochemical distributions. These results were further investigated using a random forest classifier on the basis that the geological area from which the samples were derived could be predicted based on the

lake sediment geochemistry. The random forest classifier was able to accurately distinguish geological provinces but proved less successful at accurately classifying which rock types the samples were derived from. Finally, PCA indicated that large amounts of variance within the dataset could be attributed to geologic parameters on local and regional scales specifically highlighting that substantial differences existed in lake sediment geochemistry between geologic provinces, rock types, and that interactions between rock types can produce distinct geochemical assemblages.

Natural background metal concentrations in lake sediments across the study areas were highly variable, including arsenic, which is of greatest environmental concern in the study areas. For example, 15.7% of samples had arsenic concentrations exceeding the Ontario provincial guidelines (6 mg/kg), most of which were related to watersheds with Nipissing Diabase. However, only in Nipissing Diabase dominated watersheds in the Gowganda dataset did the upper limit of background exceed the 6 mg/kg guideline. None of the natural background ranges exceeded the Canadian guideline for arsenic content in sediment for the protection of aquatic life (17 mg/kg), and the vast majority of lake sediment samples (97.2%) were below the 17 mg/kg threshold (i.e. only 2.8% of all sediment samples exceeded the Canadian objective for the protection of aquatic life). The low number of sites exceeding the Canadian objective for arsenic in sediment suggests that the Canadian objective for the protection of aquatic life is conservative and is a realistic restoration target for arsenic in lake sediments in this region post-mining.

The differences in the background geochemistry between some rock types were minimal but there were large differences between others. Most notably, samples derived from watersheds predominantly covered by Nipissing Diabase displayed elevated

concentrations of As, Ag, Sb Co, and Ni. Furthermore, in watersheds that had a mixed composition of bedrock types, that included even small amounts of Nipissing diabase, displayed enriched metal signatures, particularly for Ag, As, Sb and Co. From these empirical observations it is apparent that throughout the study area the Nipissing Diabase is one of the dominant factors influencing lake sediment geochemistry in these study areas. This result is in agreement with historical knowledge surrounding this geologic unit throughout the area, suggesting that it is a major component essential to the emplacement of the Ag-Co veins (Miller, 1908; Knight, 1922; Boyle, 1968).

The dominant geochemical controls of the Nipissing Diabase, in part, may also explain misclassified samples obtained from the random forest classifier, which had particular difficulties properly classifying rock types. These misclassified results show the impacts of mixing between co-occurring rock types in catchments and highlight that some rock types are geochemically dominant compared to others. Misclassified samples likely arose from inherent issues with rock type mixing in catchment basins with co-occurring lithologies and from underrepresented rock types in the database. It may be that in catchments with mixed lithologies there are often no clear relationships between the percentage of rock type within a catchment and the lake sediment geochemistry. Instead, catchments with mixed rock types often display a geochemical signature that may reflect a mixture of the lithologies within its catchment, and because the random forest classifier is limited to assigning one rock type to a sample there will obviously be misclassified results.

The random forest classifier may also be confused by geochemically dominant rock types which may represent small amounts of catchment area, thereby bypassing the

selection process for dominant areal extent (>70%) in the data preparation stage, but could still have a large impact on the geochemical assemblage in the lake sediments. This effect could occur due to a rock type being more susceptible to erosion, and therefore contributing more of its constituents to the lake sediments, or it may be closer to the lake and therefore less diluted during transport (Carranza, 2009). Another possibility may be that the Nipissing Diabase substantially alters the surrounding rocks within the watershed, in contact zones and fractures (associated with the intrusion) acting as conduits for hydrothermal alteration (Andrews et al., 1986). This is particularly true for the Nipissing Diabase, given the extensive nature of the sill in the region, it has substantial alteration potential beyond the contact relationships, up to 150 m (Jambor, 1971a,b), indicated by the bedrock maps. This alteration potential can be seen in the random forest classifier where the Nipissing Diabase represented the rock type that obtained the highest percentage of misclassified samples (Table 3.3).

Similarly, the Lorrain and Gowganda formations were often misclassified as Nipissing Diabase, and vice versa. The random forest classifier also highlighted that significant differences exist in the lake sediment geochemistry between the Grenville and Superior/Southern provinces where rare earth and chalcophile elements were the most important variables for delineating the relationship. Not surprisingly, principal component 2 for the Temagami region, that also separated the geologic provinces, also had high loadings for rare earth and chalcophile elements.

The PCA in both study areas showed that bedrock types are controls on lake sediment geochemistry. In the Temagami region, the PCA was able to identify that two different geological regions existed within the dataset, with component 2 separating the

Superior and Southern province to the north and the Grenville province to the south. In both the Temagami and Gowganda areas, components 3 and 2, respectively, were efficient at highlighting areas favourable for Cobalt-type mineralization, showing positive loadings for the Cobalt-type indicator elements and being spatially related to favourable geological conditions for that deposit type as well as known mineral deposits in the Mineral Deposit Index database. In the Temagami area principal component 3 also had positive loadings for Fe and Mn in addition to the Cobalt-type indicator elements. These Fe-Mn oxides can contribute to enhanced metal signatures (Couture et al., 2010) but enrichment in deeper sediments can only occur if greater amounts of those elements are present to begin with, therefore the elevated signatures can be justified. Principal component 5 in Temagami was also spatially related to the Nipissing Diabase and had positive loadings for the Cobalt-type indicator elements but had negative loadings for Fe and Mn suggesting that the variance in these areas are not completely explained by Fe-Mn oxides.

In some cases, the proximity of the Mineral Deposit Index points to lake sediments with anomalously high metal concentrations raises the possibility of anthropogenic contamination of the sites. We initially screened the dataset to remove lakes with known sources of contamination but this did not include nearby lakes that had elevated metal signatures as there was no historical record of contamination at these sites and removing those lakes would introduce subjectivity by possibly reducing the number of lakes with naturally high metal concentrations. There is the possibility though, that for lakes near mineral deposits that had milling operations, unaccounted for tailings or waste rock movement may contaminate lake sediments in nearby regions (Sprague et al., 2016).

However, the OGS sampling protocols targeted deeper sediments (20 cm depth) to reduce the likelihood of anthropogenic influences on the geochemistry signature of the sediment (in these Canadian shield lakes 20 cm of sediment deposition likely represents a time period of pre-1850; Brothers et al., 2008). Despite these efforts there is still a chance that some of the areas highlighting favourable mineralization in proximity to past producing mines are anthropogenically sourced in part because, redox sensitive elements like arsenic, under the proper conditions can be transported down into deeper sediments (e.g. a downward hydraulic gradient or rapid deposition; Nikolaidis et al., 2004; Andrade et al., 2010).

Further complicating the separation of anomalies is that several types of anomalies can exist within large databases given that the sampling medium is lake sediments. Lakes are a sink for sediments derived from areas that can be much larger in comparison to the lake itself, thus the samples are inherently controlled by the catchment basin characteristics and dependent upon the irregular nature of erosive and leaching processes taking place within them (Panahi et al., 2004). For example, a metallic vein underlying a stream in proximity to the lake may show up as a high contrast anomaly. However, if the vein being eroded was far away from the lake the anomalous signature may be masked by secondary processes during transport that reduces the chemical signature of that anomaly to one of low contrast or to background levels (Caranza, 2009). Similarly, if the source of the anomaly is covered or undergoing minimal erosion and leaching the anomaly may not show up at all. Therefore, a high contrast anomaly does not necessarily mean that area has greater mineral potential than areas displaying low

contrast anomalies because the level of the anomaly is not necessarily representative of the magnitude of mineralization in that catchment (Panahi et al., 2004).

In studies by Grunsky et al. (2013), Harris and Grunsky (2014) lake sediment geochemistry was used to positively predict bedrock types in the Melville province (Nunavut). Our results indicate that this method can be applied in the Temagami and Gowganda regions as there are clear relationships between bedrock types and lake sediment geochemistry but the same level of predictive power was not observed. Stark differences in terms of the vegetation, organic matter, biological activity, overburden and bedrock exposure between the Canadian high Arctic and our study sites suggests that higher latitude lakes have a more direct relationship between sediment geochemistry and bedrock composition compared to those in Ontario (Cameron et al., 1978). Nevertheless the value of lake sediment data collection in these terrains through large surveys, such as these, provides vast quantities of information about the geochemical landscape. These data provide valuable information that can be used as background data for restoration purposes and can be extremely useful for the target generation in exploration, especially when combined with bedrock geology maps.

The true background range of arsenic was variable throughout the study but highest in areas with Nipissing Diabase or in catchments where Nipissing Diabase was co-occurring with the Gowganda formation, where the background range was typically between 0.5 and 10 mg/kg with a median of between 3 and 6 mg/kg. However, the majority of catchments had background ranges of arsenic that were between 0.5 and 5 mg/kg with a median of between 3 and 4 mg/kg. These ranges are comparable to the Ontario regulatory standard of 6 mg/kg but are substantially lower than the Canadian

guideline of 17 mg/kg. The Canadian guidelines for the protection of aquatic life are based on short-duration laboratory experiments on plants and animals and are intended to protect aquatic ecosystems and not to represent the complexity of arsenic in natural systems. The Canadian and Ontario guidelines for arsenic offer a particular challenge as ecological restoration targets in anomalous areas such as the Gowganda and Cobalt mining camps that can have naturally high background arsenic concentrations. This study showed that naturally anomalous areas can have arsenic concentrations greater than 30 mg/kg. The Cobalt and Gowganda mining camps areas are currently subject to widespread contamination of arsenic rich tailings, up to 17,000 mg/kg (Sprague et al., 2016), which is a consequence of the lack of environmental policy on early 1900s mining practices. This study shows that geological controls on lake sediment geochemistry is substantial and specifically, we have shown that areas that have favourable conditions for mineralization (i.e. areas with mining potential) display higher levels of metals than background. With this in mind, when considering setting restoration targets for legacy contamination sites, such as those in Cobalt and Gowganda, efforts should be focused on realistic restoration targets for the background bedrock of that area, rather than a single regulatory value that may not reflect the natural conditions of the lake prior to mining.

For example, if the goal of a post-mining restoration plan is to restore the site to its natural condition, in our study regions the provincial objective for arsenic in sediments (6 mg/kg) is likely too low for a realistic restoration target given that over 15% of the sediment samples had arsenic concentrations above this objective due in part to the natural bedrock composition of their catchments. In contrast, the federal Canadian objective for arsenic in sediments (17 mg/kg) is a more realistic restoration target,

although it is likely below the anomalous values that would likely represent potential mining areas. When evaluating restoration plans for lake sediment geochemistry it is therefore important that the natural variation in background geochemistry of the region be taken into consideration.

3.5 Conclusions

Lake sediments provide valuable information on the natural variation in lake systems that are directly influenced by their catchments. Our results indicate that there is a clear connection between lake sediment geochemistry and the bedrock geology of northeastern Ontario. This was observed for both single-element background variation (for the Cobalt-type indicator elements) that are substantially different between rock types and geologic provinces and also multivariate element geochemical assemblages that were spatially related to bedrock types and provinces. Throughout the Superior and Southern provinces the Nipissing Diabase is a major control on lake sediment geochemistry as watersheds that have even minor interactions with it displayed elevated background levels, especially for the Cobalt-type indicator elements. To an exploration geochemist the geochemical assemblages represented by principal components in the PCA can be a more holistic approach for target generation as opposed to single-element maps. This research can also be valuable for environmental purposes as it provides evidence of the natural variability in background lake sediment geochemistry, which can change dramatically depending on geological properties of the area in question. In legacy mining sites where background sedimentary geochemical data were not obtained prior to mining, studies such as these can help provide realistic restoration targets that are targeted to the geological setting of the lake.

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Figure 3.1: Bedrock map for Gowganda and Temagami areas showing all the major rock units. The inset map of Ontario shows the location of the study area (grey) and towns of Gowganda and Temagami. The numbers (23d, 21c, 15, etc.) before the rock units name indicate the legend code that is referred to throughout the paper. The white dots and red squares indicate mineral occurrences and mineral deposits, respectively.

Table 3.1: Background metal concentrations for the Gowganda and Temagami datasets for arsenic, antimony, cobalt, nickel and silver for the listed rock types (e.g. 0 - 6 is the range of background, 3 is the median). Where possible, only watersheds with 75-100% of their area were used for these calculations.

Gowganda Dataset					
Rock Type	Arsenic	Antimony	Cobalt	Nickel	Silver
23d	0.5 – 10, 6	0.04-0.185, 0.11	2.04 – 11, 6.6	9.6 – 22.5, 19.35	0.04 – 0.27, 0.15
21c	0.5 – 5, 2	0.02 – 0.14, 0.07	0.63 – 7.75, 3.62	4.55 – 21.5, 15.39	0.02 – 0.14, 0.08
21d	0.5 – 4.7, 2	0.01 – 0.16, 0.09	0.11 – 11.3, 5.36	1.81 – 37.5, 23.17	0.02 – 0.155, 0.1
15	0.5 – 2.5, 2	0.03 – 0.11, 0.07	1.27 – 9.0, 5.71	8.8 – 20, 17.3	0.05 – 0.18, 0.13
12	0 – 5, 4	0.02 – 0.18, 0.12	0.67 – 8, 5.02	5.92 -39, 27.56	0.01 – 0.21, 0.1
7	0.5 – 6.5, 4	0.02 – 0.15, 0.1	0.75 – 9, 4.73	11.26 - 36.4, 24.7	0.02 – 0.13, 0.07
6	0.5 – 8, 4.5	0.02 – 0.17, 0.11	0.6 – 6, 4.44	5.92 – 40.5, 26.47	0.01 – 0.13, 0.08
5	0.5 – 8, 4	0.02 – 0.18, 0.1	0.6 – 9, 5.58	7.78 - 35, 23.68	0.02 – 0.18, 0.11
4	0.5 – 8, 5	0.05 - 0.2, 0.14	0.6 – 10, 4.07	7.78 – 54, 35.26	0.02 – 0.09, 0.09
23+21c/d	0.5 – 9, 3	0.02 – 0.17, 0.09	0.63 - 12.5, 6.475	7.15 – 27, 19.43	0.03 – 0.2, 0.13
23+15+21	0.5 – 6, 3	0.03 – 0.15, 0.08	1.27 – 9, 6.94	9.13 – 32, 20.12	0.04 – 0.295, 0.14
All	0.5 – 7, 3	0.01 – 0.165, 0.09	0.11 – 10, 5.32	1.81 – 28.5, 19.44	0.01 – 0.19, 0.1
Temagami Dataset					
Rock Type	Arsenic	Antimony	Cobalt	Nickel	Silver
23d	1.1 – 5.5, 3.2	0.03 – 0.25, 0.16	1.41 – 12, 6.89	12 – 34, 26	0.01 – 0.2, 0.12
21c	0.25 – 4.5, 2.4	0.03 – 0.18, 0.09	0.9 – 8, 5.285	8 – 25, 8	0.01 – 0.12, 0.08
21d	0.25 – 6, 3.8	0.03 – 0.28, 0.18	1.22 – 12.5, 7.895	2.5 – 35, 27	0.01 – 0.17, 0.12
15	1.5 – 4.5, 2.9	0.03 – 0.24, 0.15	1.31 – 10, 6.28	8 – 27, 23	0.01 – 0.17, 0.12
12	0.6 – 3.2, 2.2	0.03 – 0.16, 0.1	1.84 – 12, 6.56	7 – 26.5, 22	0.01 – 0.22, 0.14
7	1.4 – 4.5, 3.6	0.03 – 0.17, 0.13	2.38 – 10, 8.22	14 – 35, 29.5	0.06 – 0.25, 0.15
6	1.4 – 4.5, 3	0.06 – 0.25, 0.15	0.97 – 9, 5.76	9 – 36, 24	0.01 – 0.16, 0.11
5	1.2 – 6.5, 3.7	0.06 – 0.22, 0.15	0.84 – 10, 6.5	9 – 36, 25	0.01 – 0.27, 0.16
23+21c/d	0.7 – 7, 3.75	0.03 – 0.25, 0.16	1.04 – 12, 7.155	8 – 40, 25.5	0.01 – 0.19, 0.12
23+15	1.3 – 3.5, 2.8	0.05 – 0.16, 0.13	2.43 – 9.5, 7.52	0.03 – 0.2, 0.14	1.73 – 10, 5.92
23+15+21	1.1 – 4.25, 3	0.03 – 0.21, 0.15	2.21 – 11.5, 7.42	10 – 34.5, 22	0.01 – 0.2, 0.14
Superior	0.25 – 5.5, 3.2	0.03 – 0.2, 0.14	0.84 – 11, 6.92	2.5 – 37.5, 24	0.01 – 0.19, 0.12
GFTZ	0.25 – 3.9, 2.5	0.03 – 0.175, 0.1	0.97 – 11, 6.715	7 – 28.5, 25	0.01 – 0.19, 0.13
All	0.25 – 5.3, 2.6	0.03 – 0.2, 0.11	0.34 – 11, 6.1	2.5 – 32, 23	0.01 – 0.19, 0.11
39	0.25 – 8, 2.85	0.03 – 0.16, 0.08	0.67 – 8.5, 3.865	5 – 21, 16	0.01 – 0.17, 0.09
41	0.25 – 3.5, 1.7	0.03 – 0.17, 0.08	0.34 – 8, 4.36	2.5 – 30.5, 21	0.01 – 0.18, 0.11
42	1.1 – 5.5, 3.6	0.03 – 0.18, 0.115	2.03 – 9.5, 7.035	11 – 41, 29.5	0.01 – 0.17, 0.1
Grenville	0.25 – 4.3, 1.8	0.03 – 0.17, 0.08	0.35 – 8.4, 4.69	2.5 – 31.5, 21	0.01 – 0.2, 0.1
Gow +Tem	0.25 – 5.5, 2.6	0.01 – 0.17, 0.1	0.11 – 12, 5.825	1.81 – 32, 21.545	0.01 – 0.18, 0.11

Figure 3.2a-e: CF-curves for elements, As, Sb, Co, Ni, Ag, in watersheds whose area contained $\geq 90\%$ Nipissing Diabase (23d) in the Gowganda area. The first linear portion of the graph, up until the first inflection point is the range of background concentrations. After the inflection point the second linear portion of the graph is the range of anomalous values. The vertical red line in Figure 3.2a indicates the Canadian Sediment guideline of 17 mg/kg for the protection of aquatic life.

Table 3.2: Confusion matrix showing the amount of properly predicted samples into their respective geological province (Southern/Superior or Grenville).

	Grenville	Superior	Class Error (%)
Grenville	510	125	19.685
Superior	39	1851	2.0635

Table 3.3: Confusion matrix for the Random Forest Classifier showing the amount of properly predicted samples into their respective rock type

Rock Type	12	15	21c	21d	23d	39	41	43	5	6	7	Class Error (%)
12	1	8	2	28	4	0	33	0	1	0	0	98.7
15	0	57	21	118	16	1	12	0	6	1	0	75.4
21c	0	6	453	56	15	1	14	0	1	0	0	17.0
21d	0	16	59	785	47	0	14	0	6	1	0	15.4
23d	1	2	51	109	143	0	2	0	5	0	1	54.5
39	0	0	12	10	0	51	42	2	0	0	0	56.4
41	0	3	8	34	0	20	314	9	0	0	0	19.1
42	0	0	0	1	0	0	7	0	0	0	0	1
43	0	3	0	9	1	1	53	30	0	0	0	69.1
5	0	5	7	35	25	0	0	0	17	3	0	81.5
6	0	3	3	19	3	0	2	0	5	1	0	97.2
7	0	0	3	27	5	0	2	0	3	0	0	1
<i>No. of predictions</i>	2	103	619	1236	259	74	495	41	45	6	1	
<i>No. of misclassified samples</i>	1	46	166	451	116	23	181	11	28	5	1	
<i>Misclassified (%)</i>	50	44.6	26.8	36.5	44.8	31.1	36.6	26.8	62.2	83.3	100	

Table 3.4: Principal component loadings for Temagami center log-ratio transformed data. Bold values indicate those which are >0.1 or <-0.1.

	PC1	PC2	PC3	PC4	PC5		PC1	PC2	PC3	PC4	PC5
LOI	-0.083	-0.218	-0.230	0.117	-0.092	Mo	-0.036	-0.230	0.063	0.055	-0.259
Ag	-0.025	-0.099	-0.079	-0.156	0.199	Na	-0.121	0.076	0.012	0.196	0.065
Al	-0.016	0.163	-0.160	-0.237	0.103	Nb	-0.046	0.192	-0.206	0.126	-0.096
As	-0.072	-0.153	0.197	-0.184	0.083	Nd	0.226	0.030	-0.065	0.032	0.058
Ba	-0.068	-0.008	-0.229	0.013	-0.192	Ni	-0.109	-0.072	0.026	0.007	0.398
Be	0.046	0.057	-0.048	-0.142	-0.091	P	-0.096	0.054	-0.225	-0.238	-0.154
Ca	-0.123	-0.179	-0.055	0.193	-0.098	Pb	-0.087	-0.038	-0.017	-0.219	0.328
Cd	-0.109	-0.162	-0.147	-0.112	-0.042	Pr	0.222	0.038	-0.080	0.032	0.046
Ce	0.157	0.134	-0.170	-0.015	-0.048	Rb	-0.125	0.216	-0.072	0.151	0.047
Co	-0.027	0.070	0.193	-0.251	0.124	S	-0.085	-0.267	-0.092	0.057	-0.071
Cr	-0.058	0.241	0.066	-0.013	0.079	Sb	-0.079	-0.190	0.070	-0.188	0.215
Cs	-0.119	0.138	-0.120	0.200	0.162	Sc	0.028	-0.024	0.309	0.167	0.081
Cu	-0.047	-0.233	0.049	-0.045	0.201	Sm	0.233	0.021	-0.062	0.028	0.065
Dy	0.238	-0.005	-0.045	0.000	0.030	Sn	-0.129	-0.120	-0.138	-0.011	0.154
Er	0.230	-0.020	-0.005	-0.007	-0.009	Sr	-0.091	-0.098	-0.281	0.147	-0.090
Eu	0.228	0.004	-0.057	0.000	0.089	Tb	0.237	0.004	-0.053	0.006	0.047
Fe	-0.039	0.205	0.159	-0.231	-0.195	Th	0.013	0.031	0.313	0.227	-0.072
Ga	-0.061	0.245	-0.214	-0.045	0.020	Ti	-0.089	0.229	0.005	0.229	0.044
Gd	0.238	0.012	-0.049	0.014	0.060	Tl	-0.077	0.052	0.052	-0.065	-0.096
Hg	-0.055	-0.111	-0.224	-0.062	0.106	Tm	0.221	-0.014	0.014	-0.005	-0.027
Ho	0.235	-0.016	-0.018	-0.003	0.015	U	0.052	-0.063	-0.014	0.142	-0.051
K	-0.126	0.208	-0.078	0.081	-0.023	V	-0.044	0.160	0.065	-0.243	-0.254
La	0.196	0.035	-0.089	0.029	0.026	W	-0.065	-0.080	0.132	0.005	-0.163
Li	-0.053	0.247	0.100	0.074	0.196	Y	0.232	-0.027	0.039	-0.011	0.003
Lu	0.214	-0.029	0.063	0.021	-0.076	Yb	0.224	-0.019	0.028	0.003	-0.051
Mg	-0.129	0.187	0.097	0.182	0.113	Zn	-0.118	-0.065	0.051	-0.116	-0.202
Mn	-0.049	0.151	0.151	-0.264	-0.170	Zr	-0.044	-0.118	0.254	0.211	-0.094

Figure 3.3a

Temagami - principal component 1

Figure 3.3b

Temagami - principal component 2

Figure 3.3c

Temagami - principal component 3

Figure 3.3d

Temagami - principal component 5

Figure 3.3a-d: Principal Component Maps (a-d) for the Temagami region. The high and low values correspond to the interpolated principal component scores for all the samples after a clr transform was conducted on the raw geochemical data. The light grey lines are the geologic boundaries of the rock units shown in Figure 3.1. The total variance explained by principal components 1, 2, 3 and 5 (a-d) are 30.74%, 15.44%, 10.19% and 3.58%, respectively. The hollow diamonds and crossed hammer symbols indicate mineral occurrences and mineral deposits, respectively.

Figure 3.4a

Gowganda - principal component 1

Figure 3.4b

Gowganda - principal component 2

Figure 3.4a-b: Principal Component Maps (a-b) for the Gowganda region. The high and low values correspond to the interpolated principal component scores for all the samples after a clr transform was conducted on the raw geochemical data. The light grey lines are the geologic boundaries of the rock units shown in Figure 3.1. The total variance explained by principal components 1 and 2 are 30.45% and 13.66%, respectively. The hollow diamonds and crossed hammer symbols indicate mineral occurrences and mineral deposits, respectively.

Table 3.5: Principal component loadings for Gowganda center log-ratio transformed data. Bold values indicate those which are >0.1 or <-0.1.

	PC1	PC2	PC3	PC4	PC5		PC1	PC2	PC3	PC4	PC5
LOI	0.059	0.278	0.097	0.141	-0.065	Mg	0.145	-0.204	-0.022	0.067	-0.015
Ag	0.013	0.195	0.078	-0.160	0.272	Mn	0.050	-0.133	-0.046	-0.375	-0.168
Al	-0.080	-0.068	0.304	-0.036	-0.096	Mo	0.089	0.209	-0.142	0.018	-0.125
As	0.112	0.087	-0.133	-0.160	-0.018	Na	0.095	-0.236	0.049	0.100	0.067
Au	0.023	0.069	-0.006	0.080	0.077	Nb	0.061	-0.234	0.176	0.067	-0.119
B	0.113	0.087	-0.057	-0.071	-0.109	Nd	-0.223	-0.031	-0.030	0.030	0.028
Ba	-0.029	0.050	0.161	0.053	-0.257	Ni	0.091	0.073	-0.042	0.183	0.064
Bi	0.065	0.016	0.191	-0.067	0.304	P	0.016	0.060	0.265	-0.221	-0.219
Br	0.051	0.256	0.115	-0.036	-0.151	Pb	0.041	0.079	0.162	-0.089	0.451
Ca	0.131	0.171	-0.089	0.031	-0.141	Pr	-0.221	-0.040	-0.022	0.020	0.029
Cd	0.055	0.230	0.177	-0.076	0.036	Rb	0.102	-0.135	0.195	0.221	-0.015
Ce	-0.186	-0.109	0.098	-0.036	-0.035	Sb	0.094	0.217	-0.065	0.045	0.061
Co	-0.004	-0.035	-0.055	-0.342	0.081	Sc	0.021	-0.061	-0.304	-0.028	0.066
Cr	0.095	-0.128	-0.008	0.052	-0.061	Sm	-0.235	-0.024	-0.009	0.043	0.015
Cs	0.097	-0.053	0.096	0.332	0.082	Sn	0.083	-0.157	0.002	-0.025	0.317
Cu	-0.028	0.227	-0.082	0.006	0.194	Sr	0.043	0.171	0.132	0.183	-0.190
Dy	-0.238	0.004	0.017	0.027	-0.013	Ta	0.001	0.136	0.099	0.178	-0.045
Er	-0.234	0.017	-0.025	0.010	-0.019	Tb	-0.239	-0.009	0.007	0.041	0.002
Eu	-0.239	0.001	0.012	0.043	-0.013	Th	0.086	-0.127	-0.299	-0.003	-0.016
Fe	0.046	-0.179	-0.051	-0.339	-0.199	Ti	0.098	-0.274	0.081	0.087	-0.007
Ga	0.013	-0.175	0.302	0.059	-0.041	Tl	0.019	0.033	0.028	-0.019	-0.216
Gd	-0.238	-0.012	-0.015	0.047	0.012	Tm	-0.231	0.017	-0.037	-0.002	-0.024
Hf	0.066	0.008	-0.251	0.226	-0.012	U	-0.024	0.026	-0.098	0.203	-0.142
Hg	-0.044	0.144	0.173	0.029	-0.071	W	0.093	-0.019	-0.125	-0.074	-0.212
Ho	-0.236	0.012	-0.004	0.022	-0.018	Y	-0.232	0.012	-0.056	0.005	-0.019
La	-0.203	-0.038	-0.038	0.012	0.052	Yb	-0.229	0.016	-0.065	-0.007	-0.011
Li	0.067	-0.221	0.077	0.036	0.058	Zn	0.095	0.151	0.070	-0.189	0.045
Lu	-0.217	0.017	-0.106	-0.001	-0.014	Zr	0.107	-0.017	-0.260	0.171	-0.013

Chapter 4:

Legacy arsenic pollution of lakes in northeastern Ontario, Canada: Arsenic concentrations in lake water and sediment remains elevated nearly a century after mining activity has ceased.

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Abstract

Century old mine tailings in the Cobalt and Silver Center mining camps are widely dispersed throughout the terrestrial and aquatic environments and contain high concentrations of arsenic that pose a threat to humans and the environment. Arsenic concentrations were found to be as high as 972 $\mu\text{g/L}$ in surface waters and 10,800 mg/kg in lake sediment, which is 194 times and 635 times the objectives for the protection of aquatic life (5 $\mu\text{g/L}$ and 17 mg/kg , respectively). The mean values for arsenic in surface waters and sediment in lakes impacted by mining activity were 431 $\mu\text{g/L}$ and 1138 mg/kg , respectively, whereas lakes with no mining activity in their catchment had mean values of 2.2 $\mu\text{g/L}$ and 11 mg/kg in their water and sediment respectively. The relationship between arsenic in surface sediments and lake water is highly related ($r^2=.79$, $p<0.01$), which can have implications for natural recovery of these systems. Principal component analysis identified contaminated lakes as having different geochemical signatures than control lakes but in some cases lake sediment that was sampled below tailings in contaminated lakes, deposited pre-mining, do resemble the geochemistry of those found in control lakes. Arsenic concentrations in these samples ranged from 4.4 to 185 mg/kg , which can be considered reasonable as these areas contained abundant mineral deposits that would naturally elevate background concentrations. Even in control lakes, with no exploited mineralization, arsenic in sediment was found to be as high as 37 mg/kg at 20 cm depth, and in the geologically similar regions of Temagami and Gowganda, arsenic was found to be as high as 97 mg/kg at 20 cm depth, but more typical background values in the Superior and Southern Province are in the 6-14 mg/kg range. Even though background concentrations are naturally elevated, the presence of arsenic-

rich tailings in these lakes prevents any natural recovery from occurring. Fe-Mn oxides at the water-sediment interface perpetually scavenge arsenic from buried tailings below and from contaminated surface waters that cause arsenic concentrations to remain the highest in the upper sediments even after tailings have been buried. This process prevents any recovery of the sediment biological community that dwell in the upper sediment.

4.1 Introduction

Legacy contamination is a global environmental problem and legacy arsenic pollution can be a common result of historical mining activity in Canada (Wang and Mulligan 2006; Houben et al. 2015; Thienpont et al. 2016). Cobalt is a historical silver mining town in northeastern Ontario, Canada, named after the ‘Cobalt bloom’ (i.e. erythrite) that was famously associated with many of the major silver discoveries in the area. Mining in Cobalt began in the early 1900s with a major silver discovery that made Cobalt one of the largest silver producing regions in the world at the time. However, with declining prices for silver and cobalt, by the 1930s the majority of the mining operations shut down with the exception of some limited mining activity that continued until 1989 there has been little activity since the early days of mining. In Cobalt, silver and cobalt ore were the primary commodities, and by 1962 more than 420 million ounces of silver and nearly 11 million kg (24 million lbs) of cobalt were produced. Arsenic was intimately associated with the silver and cobalt ore and is naturally elevated in the host rock around Cobalt, however, the arsenic was not removed during processing and instead remained in the waste rock and tailings material that was dumped into nearby depressions, which were often wetlands and lakes. The arsenic associated with the waste material on the land and in lakes amounts to approximately 71,689,435 kg of arsenic in the surface environment (Thomson, 1964).

The arsenic in these legacy mine tailings remains on land, in rivers, and in lakes, and is freely migrating throughout the environment today (Sprague et al., 2016). In the Cobalt region, arsenic concentrations in tailings can vary greatly depending on the location and the enrichment processes occurring but are orders of magnitude greater than

Canadian environmental guidelines. Generally speaking, documented studies from the Cobalt area have found arsenic concentrations in tailings to be anywhere between 417 and 17,900 mg/kg with typical values being between 800 and 1500 mg/kg (Hawley 1980; Dumaresq 1993; Sprague et al., 2016). The surface water concentrations of arsenic are typically an order of magnitude lower than sediments but still far above water quality and aquatic standards, which is 5 µg/L for the protection of aquatic life (CCME 2001; Sprague et al., 2016).

Although it is not disputed that historical mining activity has increased arsenic concentrations in certain lakes around Cobalt, determining natural arsenic concentrations in lakes in the Cobalt region is complicated because the lack of long-term environmental data and on-going migration of the tailings material and contaminated water (Sprague et al., 2016). Further complications arise due to the primary element of concern, arsenic, being a redox sensitive element that is highly mobile, especially under reducing conditions, that has the ability to migrate in soils and lake sediments (Nikolaidis et al., 2004; Andrade et al., 2010). The properties of arsenic are complemented by the redox profile encountered in lake sediments. Lake sediments are typically oxidizing in surface waters and at the water-sediment interface and are reducing below this zone (Couture et al., 2010). This redox profile is an important consideration because it promotes mobilization of metals after burial, which ultimately alters the stratigraphic profile for these elements with most of the movement of arsenic being upward to the sediment water interface (Andrade et al., 2010). The process of remobilization during burial is, however, not a complete one, therefore sampling deeper sediments (>20 cm) (Takats and Dyer, 2004) can yield estimates of arsenic that are closer to background levels.

Lakes act as integrators of watershed scale processes and serve as an effective trap for these surficial sediments as they accumulate coarse and fine sediments from the streams and rivers flowing through their catchment (Cameron, 1977; Cameron, 1978; Panahi et al., 2004). The geochemical assemblage of lake sediments is derived from constituents of primary rock forming minerals, secondary precipitated minerals formed through weathering, minerals typical of mineralization, and dissolved ions in surface waters that adsorbed to clays, Fe-Mn oxides and organic matter (Rose, 1975; Panahi et al., 2004). Sampling lake sediments represents a practical approach by which a singular sediment core can represent an extremely large area (Smol, 2008). Additionally, the stratigraphic nature of lake sediments, their direct relationship to their surface waters, and relatively low sedimentation rates provide a medium that allows the study of the current state of the environment as well as geochemical and biological changes throughout time (Smol, 2008). This is particularly useful for investigating background conditions and the magnitude and rate of human disturbance on aquatic ecosystems.

The objectives of this study were first to quantify arsenic concentrations in lake water and surface sediments of contaminated and uncontaminated lake systems in the Cobalt region of Northeastern Ontario to determine the spatial extent and magnitude of legacy arsenic contamination in the region. The second objective was to examine probable background concentrations of arsenic in contaminated lakes as potential realistic restoration targets for these sites. To estimate background arsenic concentrations for contaminated sites three approaches were considered; 1) a space for time substitution based on the uncontaminated control lakes in the Cobalt region, 2) results of a landscape scale analyses of lake geochemistry from thousands of lakes located in similar geology

(Sprague and Vermaire submitted), and 3) a down-core analysis of pre-mining arsenic concentrations in the sediment cores of contaminated lakes. Overall, this study provides important details on the current magnitude and spatial extent of one of Canada's largest arsenic contaminated regions while recommending realistic restoration targets for arsenic in these contaminated lakes.

4.1.2 Study area

Sampling sites were located south of the Town of Cobalt and around the smaller mining camp of Silver Center in Northeastern Ontario (Figure 4.1). The sampling locations were all east and north of the Montreal River and to the west of Lake Temiskaming. All of the drainage in the area eventually makes its way into the Ottawa River. Although Silver Center is no longer populated the Town of Cobalt remains a vibrant community with a population of approximately 1100 residents. Cobalt was named as Ontario's Most Historic Town in 2001 and is listed as a Canadian National Historic Site by Parks Canada for the importance of Cobalt to the history and development of the mining industry in Canada.

The Cobalt mining area occurs along the north and northeastern margins of the Cobalt Embayment, part of the Huronian Supergroup, which is in contact with isolated inliers of Archean aged basement rocks (Andrews et al., 1986). The oldest rocks in the study area are the Archean volcanics. Younger granitic rocks intrude into these Archean basement rocks. Unconformably overlying the Archean volcanics and granites is the Gowganda formation, which is a variable unit that is characterized by conglomerate, arkose, greywacke, and argillite (Thompson, 1964; McIlwaine, 1970; Jambor, 1970). Conformably overlying the Gowganda formation is the Lorrain formation, which is a

quartz to feldspathic arenite that contains beds of pebble conglomerate (Thompson, 1964; McIlwaine, 1970; Jambor, 1970). Intruding all of these units is the Nipissing Diabase, a large (continuous in parts) mafic sill that provided the heat engine and fracturing of country rock necessary for the deposition of the high-grade silver veins (Miller, 1908; Knight, 1922). The silver veins are typically found in contact areas between the Nipissing sills and rocks of Gowganda and Archean volcanics but some silver has been mined from the Diabase itself (Miller, 1908; Knight, 1922; Andrews, 1986). The veins are sometimes pure silver but often were associated with large amounts of cobalt and arsenic, and lesser amounts of nickel, copper and antimony in a gangue material of calcite (Boyle, 1968; Andrews, 1986). The tailings are composed of the residual fraction that is left over from the milling and refining processes. This would include a suite of the metallic ore minerals listed in Table 2.1 as well as minerals contained in country rock, adjacent to ore material but not ore itself. Some of which would have undergone some K-feldspar, chloritic and epidote alteration during the emplacement of the veins (Jambor, 1971). Ground up country rock in the tailings and their associated mineralogy would include Nipissing Diabase (Quartz Gabbro; quartz, olivine, plagioclase feldspar, amphibole, pyroxene and biotite), Archean mafic volcanics (basalt, andesite; quartz, plagioclase feldspar, amphibole, biotite) and the Gowganda formation (conglomerate, greywacke, arkose, siltstone; mixed mineralogy of quartz, Na-K feldspars and mafic minerals). A weak chloritic alteration also exists in many of the country rocks, particularly the mafic volcanics, and makes up a minor component of the minerals within the tailings. Dolomite and calcite are also abundant in the tailings as they made up a large portion of the vein material (Dumaresq, 1993).

4.2 Methods

4.2.1 Field sampling

Water and sediment sampling took place in the summer of 2015. A total of 25 lakes were sampled that targeted 13 contaminated and 12 uncontaminated (control) lakes. Contaminated lakes were sampled to assess the current contaminant levels in lakes adjacent to mining operations whereas uncontaminated lakes were sampled to establish variances in background metal concentrations for lakes in the region. In each lake, a temperature, pH, conductivity, and dissolved oxygen profile was taken using a YSI Professional Pro series multimeter and a water sample was collected for total metals analyses at a depth of approximately 20 cm below the water's surface. Water samples for metal analyses were kept refrigerated at 4°C at the field site and shipped to Caduceon Environmental Laboratories in Ottawa, Ontario, for metal analyses.

Lake sediment cores were taken from near the center of each lake using a gravity corer. Lake sediment cores were taken at the maximum depth (typically the center of the lake) to obtain sediment that best represents whole catchment processes. Efforts were made to collect sediment cores greater than 20 cm in length, however, in some of the contaminated lakes with substantial tailings deposits in the bottom of the lakes it was difficult to obtain a longer sample. In the field the sediment cores were measured, visible stratigraphic changes noted, and the cores were subsampled at 1 cm intervals. Sediment samples were shipped back to Carleton University and stored at 4°C until analyzed in the laboratory. The lake sediment and surface water concentrations were compared to both Canadian and Ontario regulatory standards.

4.2.2 Laboratory analyses

To estimate the water, organic, and mineral content of the sediment core loss on ignition was completed at 1 cm intervals for each of the sediment core. Loss on ignition followed standard procedure (Heiri et al. 1999). Briefly, water content was determined for each sample by measuring the weight loss of 1 cm³ sediment sample following heating of the sediment for 24 hours at 110°C. Similarly, the percent organic content of the sediment was determined by the weight loss of the sediment following heating to 550°C for 4 hours. Any material after loss on ignition for water and organic content was presumed to be mineral content.

For the uncontaminated lakes, sediment geochemistry was conducted on the surface sediments, at 20-25 cm depth, and at the bottom of the sediment core for each core. For contaminated lakes, containing visible tailings in their sediment record, a more detailed sampling protocol was undertaken. For these lakes geochemistry was conducted on the surface sediments in addition to sediment above, below and in the tailings. If the bottom sediment was organic material instead of visible tailings it was also analyzed. Surface water samples for total metals were unfiltered, preserved in a 0.5% HNO₃ acid, and kept cool and void of oxygen prior to analysis. The metals of interest for this study were selected based on their relationship to the Cobalt metallic ores and their potential for environmental harm. The geochemical analyses were carried out using Induced Couple Plasma – Mass Spectrometry (ICP-MS) for samples with low metals, and ICP - Atomic Emission Spectrometry (ICP-AES) for samples with high metal concentrations. Sediment and tailings samples were prepared by using 0.3 g of sediment (fine fraction <0.355mm) were digested in an aqua regia solution using 1 mL of HNO₃ and 3 mL of HCl. They

were heated at 100°C for 2 hours then diluted with 30 mL of reagent grade water and thoroughly mixed. This method releases metals that would be considered “environmentally available” as opposed to total metals in the sample. The elements selected for detailed study included arsenic, antimony, cobalt, nickel, and silver. Both the sediment and surface water samples were analyzed at Caduceon Environmental Laboratories in Ottawa, ON.

4.2.3 Obtaining Background Samples and Statistical Analyses

In addition to establishing the current concentrations of metals in the contaminated and uncontaminated lakes the reliability and validity of the results from three approaches for establishing natural arsenic conditions were investigated in this study. The first approach for establishing background concentrations of metals was simply to sample metal concentrations below the contaminated sediments. This is the simplest method of determining natural arsenic concentrations and reduces variability of metal concentration due to inter-lake differences in morphometry and catchment characteristics but the mobility of arsenic and other metals in reducing and saturated conditions to move up and down core may limit the usefulness of this methodology (Nikolaidisa et al., 2004; Andrade et al., 2010; Couture et al., 2010). The second approach relied upon a fundamental assumption that lake sediment geochemistry is largely controlled by the bedrock composition in the lakes catchment, this relationship has been demonstrated in southern Nunavut’s boreal forest (Harris and Grunsky, 2015), Nunavut high arctic (Grunsky et al., 2014) and adjacent areas of Temagami and Gowganda (Panahi et al., 2004; Sprague and Vermaire, submitted). The second method uses non-contaminated (control) lakes of the same, or similar, catchment geology in the

Cobalt and Silver Center areas to establish a range of background arsenic values for the contaminated lakes, where possible catchments with documented mineralization were selected. A concurrent project (Sprague and Vermaire, submitted) examined historical sediment records collected by the Ontario Geological Survey (OGS) from the nearby areas of Gowganda and Temagami (Hamilton, 1997; Takats and Dyer, 2004) and established the range of background and anomalous concentrations in lake sediments for the major rock types in the study areas. Because the rock types and mineral deposits (especially those in Gowganda) are similar to those in Cobalt, the background concentrations of metals from the Temagami and Gowganda areas are used as the third approach for establishing background conditions in the contaminated lakes of Cobalt. Cumulative frequency curves (hereafter termed CF-curves) were used as a statistical approach to determine the natural range of background conditions. The inflection point separates natural anomalous values from the range of background variation and in most cases is a well define break in the linear portion of the graph (Reimann et al., 2005; Matchullat et al., 2009; Wei and Wen, 2012).

To investigate changes in the multivariate metal concentration data for both the water and sediment samples principal component analysis (PCA) was carried out using R base package (R Core Team, 2016). Before the PCA was conducted metal concentrations were center log-ratio transformed to correct for closure and non-normal sample distribution using the robCompositions package (Templ et al., 2011) in R. PCA was selected because it is a versatile multivariate statistical method, commonly used in geochemical studies, which can reveal complex inter-relationships that exist between samples. For example, PCA can help to identify groups of samples (i.e. different geologic

regions (Grunsky et al., 2014)), identify geochemical processes (Cheng et al., 1997), identify sources of contaminants (i.e. natural or anthropogenic (Borvůka et al., 2005; Zaharescu et al., 2009; Sprague et al., 2016)) and biological studies (i.e. the impacts of mining on biological communities (Kihlman et al., 2010; Hyden et al. in prep). PCA conducted on the lake sediment included all the elements in the geochemical analysis (for a list see Table 4.4). PCA conducted on the water samples included all the geochemical analysis (for a list see Table 4.2). Ellipses outline the 95% confidence interval of the centroids for the lakes that are influenced by mining activity (contaminated and migration lakes) and control lakes not influenced by mining activity were added to the PCA graphs to highlight the separation of samples.

4.3 Results

4.3.1 Arsenic in surface waters

The location of sampled lakes and the concentration of arsenic in surface waters can be seen in Table 4.1; more detailed field and geochemical data can be seen in Table D-1 and Table D-2, respectively (Appendix D). As expected, there was a clear separation between contaminated lakes and control lakes, especially for the elements associated with Cobalt-type mineralization. The maximum concentration of arsenic came from Cart Lake at 972 µg/L (Table 4.1), whereas the mean and median concentrations of arsenic for contaminated lakes was 431 and 348 µg/L, respectively (Figure 4.2). The sample from Cart Lake is 97 times greater than the drinking water standard of 10 µg/L and 194 times greater than the objective for the protection of aquatic life of 5 µg/L (CCME, 2001). All of the surface water samples from heavily contaminated systems exceeded drinking water standards by at least 8 times and were 16 times greater than the objective for protection of

aquatic life. Nearly all the control lakes (with the exception of Silver Lake; arsenic concentration of 7.3 µg/L) had arsenic concentrations that were below the limit for the protection of aquatic life (Table 4.1). The lowest sampled arsenic concentration came from East Pine Lake at 0.4 µg/L whereas the mean and median values for arsenic concentrations in the control lakes were 2.2 and 1.7 µg/L, respectively. The mean value of arsenic concentrations in the surface water for the contaminated lakes was 196 times the mean value of arsenic concentrations in the surface water of control lakes. Lakes impacted by tailings migration or effluent from tailings areas often displayed values that were between the two extremes of contaminated and control lakes, with median and mean arsenic concentrations of 36.6 and 55 µg/L, respectively (Figure 4.2). Metals from contaminated lakes were also found to contain elevated concentrations of antimony, cobalt, sulphate and nickel in comparison to the control lakes (Table D-2; Appendix D).

The PCA on surface waters was highly effective at separating lakes that are contaminated from those that are not (Figure 4.3). Principal component 1 (explained 30% of the variation) and principal component 2 (21% of the variation) combined to explain 51% of the total variance in surface water geochemistry among samples. Axis one of the PCA was largely a separation of control lakes from contaminated sites with contaminated associated with greater concentrations of arsenic, antimony, cobalt, and molybdenum. Control lakes in contrast were associated with greater relative concentrations of silver and aluminum (Table 4.2). The PCA was also useful at grouping lakes impacted by tailings migration or tailings effluent (green dots; Figure 4.3) between the groups of control and contaminated lakes, likely because these lakes often display intermediate values between control and contaminated sites. Note that for this relationship Crosswise Lake was

sampled upstream from major historical mining activity, which may be why it resembles a migration lake, because the impacts of mining were reduced on the upstream side of the lake. Tooth Lake is similar in this respect as it doesn't contain tailings waste but receives effluent from waste rock in its catchment.

4.3.2 Relationship between surface waters and lake sediment

There is a strong relationship between the arsenic concentration in surface water and surface sediments in the study lakes ($r^2=0.7919$, $p<0.01$) (Figure 4.4) but arsenic concentrations in the surface sediment are generally an order of magnitude greater than the water. For contaminated lakes whose surface sediments are tailings there is likely exchange between the water column and the tailings, which can contribute to this relationship, especially if the redoxcline is above the water-sediment interface (Andrade et al., 2010; Kihlman and Kauppila, 2010). This was particularly evident at New Lake, where a beaver dam blocks tailings from physically migrating downstream, and no tailings were detected in the lake sediment. Yet, concentrations of arsenic in surface sediments and surface waters at the sample locations of North and Middle New Lake were substantially higher than nearby lakes (Figure 4.5; Table 4.3). In New Lake, surface water arsenic concentrations were 21 times the median arsenic concentration value found in control lakes and arsenic concentrations in surface sediments were up to 40 times more enriched than arsenic in surface sediments of control lakes. The high concentrations of arsenic can likely be attributed to dissolved arsenic effluent from the contaminated catchments upstream (containing Ibsen Pond and Brady Lake) that penetrate the dam and flow downstream into New Lake. This site importantly demonstrates that effluent from

contaminated areas can have equivalent deleterious effects on the lake environment as physical tailings migration.

4.3.3 Geochemistry of sediment

Contaminated lakes

The results of the sampling program targeting contaminated lakes were variable with respect to the concentration of arsenic (and related elements) in tailings layers and in lake sediment below these layers (Table 4.3; Figure 4.5). In Table 4.3 the samples within tailings layers are clearly identified by the high concentration of arsenic, antimony, cobalt, nickel, silver and low organic content of the sample. The maximum concentration of arsenic obtained in the sampling program was from Cobalt Lake where the arsenic concentration in the surficial lake sediment was 10,800 mg/kg, which is 635 times the regulatory objective of 17 mg/kg (probable effect level, CCME, 1999). The mean value for arsenic concentration in lake sediments influenced by mining activity was 1138 mg/kg (67 times the federal objective) whereas the median concentration was substantially lower at 315 mg/kg (18.5 times the objective). The median and mean were lowered by samples below tailings layers that are closer to background values. Within the samples that are clearly influenced by arsenic enrichment (either directly by mining or through mobilization) the median arsenic concentration in the sediment was 1090 mg/kg and the mean was 1779.7 mg/kg. For contaminated lakes, arsenic concentrations in tailings are typically within the 1000-3000 mg/kg range (Figure 4.6 a,b).

4.3.4 Background Concentrations

4.3.4.1 Samples Below Tailings Layers in Contaminated Lakes

Sediment from contaminated lakes below the tailings layers did contain (Table 4.3; Figure 4.5) some samples, which appeared to be near background levels. These sediment cores include samples from Ibsen Pond, Brady Lake, Kirk Lake, South Peterson Lake, North Peterson Lake, Cart Lake, Fourclaim Lake, Kerr Lake, New Lake, Maidens Lake, Tooth Lake and Crosswise Lake (Figure 4.5). These samples are identified by their lower arsenic values, relative to the tailings above them, and higher organic content (Table 4.3). Low silver concentration (<3.5 mg/kg) also acted as a valuable tracer for the presence of tailings in these lakes due to its comparatively greater abundance in tailings (>10 with a mean of 102 mg/kg) (Table 4.3) and low mobility of silver compared to arsenic, especially in organic rich material under alkaline conditions (Boyle, 1968). Using samples from these cores (excluding surface samples), the range of probable sediment arsenic concentrations was between 4.4 to 185 mg/kg, with a mean of 77 mg/kg and median of 61.5 mg/kg.

4.3.4.2 Control lakes

The average values of arsenic, antimony, cobalt, nickel and silver in control lakes at depths of 1 cm, 5 cm, 20 cm and 60 cm were substantially lower than those found in contaminated lakes (Figure 4.7). The average organic and water content of control lakes was also higher than those in contaminated lakes (Figure 4.8). From control lakes the maximum value of arsenic obtained was a surface sample from Green Lake and had a value of 109 mg/kg (Table 4.3). This surface sediment sample was taken near a fault and

therefore may be influenced by groundwater enrichment that is compounded by metal scavenging Fe-Mn oxides. With surface samples included the background concentrations of arsenic in the sediment of control lakes range from 0.5 to 109 mg/kg, with a median of 6.7 and a mean of 11 mg/kg (Table 4.3). Through redox cycling the concentration of arsenic in surface sediments can be enriched, causing them to exceed objectives for the protection of aquatic life, in addition to skewing the background values substantially. In total, 13% of the samples from control lakes exceeded the objective of 17 mg/kg and 66% of those were from 0-1 cm depth. Excluding the surficial sediments the maximum concentration of arsenic in the control lake sediment was 37 mg/kg with a median of 4.1 mg/kg and a mean of 6.4 mg/kg, which is well below the probable effect level of 17 mg/kg for the protection of aquatic life (CCME, 1999). Within the control lakes there are two distinct sub-populations of background arsenic concentrations in sediment (Figure 4.9a), those whose range of values were between 0.5 and 5 mg/kg and those between 5 and 15 mg/kg. Most of the samples with arsenic concentrations greater than 15 mg/kg were from surficial sediments (Table 4.3). Samples from the lower range (0.5-5 mg/kg) were sampled from lakes where documented mineralization was minimal, whereas samples obtained from the 5-15 mg/kg range were from lakes whose catchments had favourable geological conditions for mineralization. Using the cumulative frequency-curve (CF-curve) approach the natural variation in background conditions for the control lakes was determined to be 0.5 to 14 mg/kg (Figure 4.9b). Anomalous natural background values can range from 14 – 110 mg/kg but samples occurring in this range were mostly related to probable Mn-Fe oxides.

4.3.4.3 Principal Component Analysis of Sediment

The PCA conducted on the lake sediment geochemistry was effective at separating lakes influenced by mining activities from those that were not (Figure 4.10). With principal component 1 (44%) and principal component 2 (21%) combining to explain a total of 66% of the variance in lake sediment geochemistry. For component 1 the variables that were important for separating the contaminated lakes from the control lakes, with a positive relationship, were primarily those related to Cobalt-type mineralization; arsenic, silver, cobalt, lead, nickel and cadmium (Table 4.4). Component 1 was also effective at identifying lakes that have been impacted by migration of tailings or effluent from tailings deposits. These lakes included Kirk Lake, New Lake, Maidens Lake, and Ibsen Pond. These lakes plotted in-between the two extremes of control lakes and contaminated lakes. Additionally, some of the samples taken from below the tailings layers in contaminated lakes also plot within the 95% confidence interval of the centroid for control lakes, suggesting that these samples may reflect background conditions prior to contamination. These include samples from South Peterson Lake (41, 59 cm), North Peterson Lake (38 cm), Fourclaim Lake (25, 48 cm), Crosswise Lake (20 cm), Kirk Lake 1 (20, 29 cm), North New Lake (20, 39 cm), Middle New Lake (57 cm) and Brady Lake (19, 40 cm). For these samples, the arsenic concentrations range between 4.8 and 177 mg/kg with a mean and median of 61 mg/kg and 43 mg/kg, respectively. Cart Lake (30 cm), South Peterson (63 cm), Kerr Lake (6 cm), Tooth Lake (2, 3, 5 cm), Crosswise Lake (36 cm) and Middle New Lake (20 cm) also plot close to the 95% confidence interval centroid of the control lakes and may also represent suitable background samples.

Principal component 2 was also useful for separating groups of samples and explained 21 % of the variance (Figure 4.10). PC2 was notably effective at separating extremely contaminated samples from those that are less contaminated or pristine. Component 2 showed some ability to group lakes with similar catchment geology, particularly for lakes whose catchments included Nipissing Diabase co-occurring with Granite and for catchments with Gowganda formation.

4.3.4.4 Background variation from the Temagami and Gowganda areas

Data from the Temagami and Gowganda areas were collected by the OGS at sample depths of 20 cm (Figure 4.11a). The CF-curve shows that the upper limit of the natural background variation is 6 mg/kg and represents 80% of the data (Figure 4.11b). This data is comparable to the control lakes sampled in this study whose watersheds were not influenced by mineralization and represents the natural background for those lakes. The inflection point for the first linear portion of the graph (Figure 4.11b) is less than half of that of Cobalt, which confirms the unique geological conditions for that area. However, after the first inflection point the change in slope is gradual until the CF-curve becomes horizontal, reaching 24 mg/kg. This represents the majority of natural anomalous variation (related to mineralization) and this range is similar to the background determined in control lakes from Cobalt. In concurrent research, using the data from the Temagami and Gowganda areas (Chapter 3 this thesis), in catchments with favourable geologic conditions for Cobalt-type mineralization the natural anomalous concentrations for arsenic can be as large as 97 mg/kg. As the Cobalt area had a large amounts of Cobalt-type mineralization that is intimately associated with arsenic, it is

plausible that natural arsenic concentrations in lake sediment from the Cobalt area could be as high as 97 mg/kg if not greater.

4.4 Discussion

This study investigated the current and paleo-geochemical conditions in lake environments from the historical and prolific silver mining camps in Cobalt and Silver Center, ON. This new data from the Cobalt area investigated lakes that have been heavily impacted by mining, moderately impacted, impacted by downstream migration of tailings and contaminated waters, as well as control lakes that have not been influenced by mining activity. Our results indicate that arsenic contamination in these aquatic environments is just as severe, and in some cases more severe, than previous studies that focused primarily on terrestrial arsenic contamination (Dumaresq, 1993; Sprague et al., 2016). Our results also indicate that the geochemical background in Cobalt is substantially higher than adjacent areas, and far greater than regulatory standards. The impacts of mining in the early 1900s in the Cobalt area are still being felt today, and are especially alarming given the widespread and extreme nature of arsenic contamination throughout the area. Cobalt, Ontario, represents one of the oldest, largest, and most severely impacted areas affected by legacy mine (arsenic) contamination in Canada.

The gangue (the vein host mineral) material for the ore in the region was calcite and acts as a pH buffer in the tailings, making them slightly alkaline and not acid producing (Sprague et al., 2016). The geochemical focus of this paper is on arsenic due to the high concentration of arsenic in comparison to other elements in the tailings and lake sediment as well as it being the element of greatest environmental and toxicological concern in the region. The majority of tailings in lakes throughout the Cobalt mining

camp are located adjacent to the mills that processed the ore. Migration of tailings from these locations is substantial and controlled by the streams and creeks that run through the low-lying tailings deposits, transporting them downstream. Previous work (Sprague et al, 2016), and this thesis, can verify that even small streams have the potential to transport large amounts of arsenic rich tailings downstream over time (e.g. Ibsen Pond and Kirk Lake). Even if physical barriers exist (e.g. beaver dams) effluent from tailings deposits can significantly alter surface water and lake sediment geochemistry in lakes downstream. This lack of containment has led to the contamination of several lakes in the area that had no mining activity on them (New Lake, Ibsen Pond, Kirk Lake).

In this study we have shown that arsenic sampled from the sediment of contaminated lakes greatly exceeds regulatory standards by at least a factor of 18.5 times but as high as 635 times the regulatory limit of 17 mg/kg (CCME, 1999; probable effect level). Surface waters from these lakes also contain alarming concentrations of arsenic and are far above the guidelines for safe drinking water and protection of aquatic life (CCME, 2001; Health Canada, 2014). These regulatory limits are determined by the government bodies as a minimum threshold to prevent harm to human life and aquatic life (OME, 2008, 2011; CCME, 1999, 2001). Some lakes that were initially selected as controls, because they were substantially downstream from mining activity, were also found to contain alarming amounts of arsenic in both surface waters and sediment. This confirms what previous studies (Dumaresq, 1993; Sprague et al., 2016) have postulated; that the migration of tailings, and associated waste waters, are substantial and impact an area disproportionately larger than the area of the waste itself. A great example of this can be found at Kirk Lake, where on-going migration of tailings from the Beaver Mine

forms a deltaic deposit along the shoreline of Kirk Lake (Sprague et al, 2016).

Unbeknown without this research, is that the migration of tailings impacts a significantly larger area in the lake; a curtain of tailings cover nearly the entire lake bottom with arsenic concentrations that can exceed 3600 mg/kg. This was also evident at Ibsen Pond and New Lake where the tailings in the drainage area have impacted lakes downstream that account for a lake area that is approximately 7.3 times larger than the area of the tailings; not considering un-sampled lakes farther downstream that are likely influenced as well.

In many ways, our findings in Cobalt are similar to the recent and current studies focusing on the arsenic contamination at Giant Mine near Yellowknife, NT.

Comparatively, Cobalt has received marginal scientific and media attention. At the Giant Mine arsenic contamination is attributed to both physical migration of tailings into Yellowknife bay (Andrade et al., 2010), as well as airborne contamination from the roasting process (Houben et al., 2016). At the Giant Mine site samples from the mill can contain up to 40,000 mg/kg arsenic while arsenic in sediment cores from the mine as well as downstream were found to be less than 3670 mg/kg. In Yellowknife bay, submerged tailings were found to be as high as 3685 mg/kg but were typically in the 1000 mg/kg range (EBA, 2001; Golder, 2002; Andrade et al. 2004). Similar samples obtained from a mill in Cobalt had arsenic concentrations in excess of 218,000 mg/kg (Dumaresq, 1993), and lake sediment samples of tailings material in contaminated lakes can be anywhere from 470 to 10,800 mg/kg, but are more typically between 1500 and 2500 mg/kg.

Arsenic in surface waters from the control lakes are typically below the regulatory limits for drinking water and for the protection of aquatic life (CCME, 2001; Health

Canada, 2014). However, arsenic in heavily contaminated lakes, and even lakes influenced by downstream migration, contain arsenic that greatly exceeds background levels and regulatory standards (Figure 4.2). These waters flow out of the area into Lake Temiskaming, the head water for the Ottawa River, where an estimated 18,000 kg of arsenic is released each year (Dumaresq, 1993). The arsenic speciation in surface waters of Cobalt area are typically (85%) in the oxidized form As(IV) but As(III) does exist, and is more prevalent in groundwaters (Percival et al., 2004). Between the surface sediments and arsenic in surface waters, there is a positive relationship ($r^2=0.79$, $p<0.01$) with an order of magnitude decrease in concentration of surface waters compared to sediment (Figure 4.4). This relationship is significant because contaminated sediment and surface water can act as a source of arsenic to previously uncontaminated systems. Tailings migrating away from source can act as a source of arsenic to surface waters, as in the case of Kirk Lake (KRR-3 Figure 4.1). Also, arsenic-rich effluent flowing through catchments with mine tailings into areas where no mining occurred can act as a source of arsenic for surface sediment. This was evident at New Lake where no tailings were observed, but high arsenic concentrations in waters and sediment were found. This process of enriching surface sediment via surface waters, and vice versa, can be attributed to Mn-Fe oxides that scavenge metals under oxidizing conditions at the water sediment interface. Upon burial these oxides undergo reductive dissolution and release the previously scavenged metals to pore waters that return to the water sediment interface to be scavenged again. This redox loop perpetually enriches surface sediments with arsenic, which can have substantial biological implications for remediation and recovery of the inflicted lakes.

In the ice-free months the majority of our study lakes become thermally stratified and these seasonal changes can have an impact on the mobility of arsenic. In a similar study, Andrade et al. (2010) speculated seasonal variability may have an impact on arsenic mobilization because in summer and fall months the redoxcline can be found 2-3 cm above the water sediment interface; this would inhibit surficial Fe-Mn oxides from scavenging upward migrating arsenic released from the submerged tailings below. A similar study on mining impacted Balmer Lake, Northwestern Ontario, also noted that seasonal variability could significantly impact arsenic release during summer and fall months when reducing conditions can be found near the water sediment interface (Martin and Pedersen, 2002). This study also showed that evolution of the lake, with reduced anthropogenic inputs, actually resulted in more arsenic release over time (Martin and Pedersen, 2002). They attributed this to increases in oxygen demand in the near surface sediments due to increased organic content that promoted reductive dissolution of Fe-Mn oxides and release of metals (Martin and Pedersen, 2002). This is also observable in Cobalt, as nearly a century of non-mining has not resulted in recovery of these lake ecosystems, especially from a geochemical perspective. In fact, many of the lakes display the highest concentrations of arsenic in surficial sediments (Table 4.3). Seasonal variability wasn't assessed in our study, but the redoxcline did not appear to be above the water sediment interface, however it was not assessed at the cm scale necessary to pinpoint its location. If reducing conditions are found above the WSI, reductive dissolution of surficial Fe-Mn oxides could be releasing significant metals to surface waters. Under these conditions, submerged tailings would act as a source of arsenic to surface waters, especially during ice-free months when biological activity is at its greatest.

In terms of determining realistic background arsenic concentrations for contaminated lakes, there were some differences in the three different methods we applied. Each method comes with its limitations; samples from Temagami, Gowganda and control lakes do not necessarily represent mineralized areas, and samples below tailings are potentially influenced from sediment and tailings above them. That being said, the background concentrations of arsenic from control lakes were <14 mg/kg, while background from the nearby, and geologically similar, areas of Temagami and Gowganda had the lowest background values, at <6 mg/kg; less than half of that of control lakes from Cobalt. This suggests that background arsenic concentrations are naturally elevated in Cobalt as a result of the unique geology. However, these areas were not exploited for their mineral potential and likely represent a “low” background compared to the values you would expect to find in lakes adjacent to the Cobalt mining area that were exploited for their mineralization.

Taking into account the immense high-grade ore that was found in the Cobalt area (more than 420 million ounces), one can presume that the Cobalt area, and especially lakes close to ore deposits, would have anomalously high arsenic values compared to natural background of lakes at the landscape scale. Therefore, it seems appropriate to use naturally anomalous values that exceed the normal background variation to put the Cobalt area into context. From the Gowganda and Temagami area this naturally anomalous variation, that is not influenced by anthropogenic activities or Mn-Fe oxides (being sampled at 20cm depth), can be as high as 97 mg/kg. These values were obtained from areas that have a substantially reduced mineral deposit potential in comparison to Cobalt. Taking this into account, the arsenic concentrations obtained in lake sediment from below

tailings layers in contaminated lakes do appear realistic, albeit there is a chance that they have been increased by tailings deposited above the sample. When using samples from contaminated lakes that had low silver concentrations, high organic content and no visible tailings, arsenic concentrations from lake sediment sampled below tailings layers were as high as 185 mg/kg with a mean and median concentrations of 79 and 59 mg/kg, respectively. Giving weight to all methods, a reasonable, and flexible, estimate of natural background variation in the Cobalt area could be somewhere in the 100 – 200 mg/kg range.

Restoration efforts in the Cobalt area are complicated because the contamination is so extensive and severe. Extensive surveying would be required to locate all of the waste before any meaningful discussions of remediation could be made. In Cobalt, restoration efforts are also complicated because the majority of the mining companies that created the waste no longer exist and followed standard mining practices over a century ago. Natural recovery of these systems is unlikely, given that arsenic concentrations remain highest at the water-sediment interface due to Mn-Fe oxides that perpetually enrich arsenic concentrations in surface sediments from dissolved arsenic sourced from surface waters and buried tailings below. This was most evident at Ibsen Pond, where tailings were located at mid core levels but the highest concentrations of arsenic were actually found in the surface sediments. For the sediment biological community, which prefer these surface sediments, this has obvious negative implications for recovery.

Recommendations for future research in this area should focus on the mechanisms of arsenic release to determine if tailings in lake sediments are a major

source to the arsenic in surface sediments and surface waters or whether terrestrial tailings are the major source. Column experiments using lake sediment and tailings from Cobalt could be used to model this mechanism under saturated conditions. Similarly, column experiments in un-saturated conditions with periodic wetting could be used to model arsenic release from tailings above the water table. This research could greatly benefit remediation strategies for the region. Accurate measurements of the redoxcline in these lakes to determine if it is located above or below the WSI could shed light on whether submerged tailings act as a source of arsenic to surface waters, and if seasonal changes influence arsenic release. Waste rock on the mine sites may also be a significant source of arsenic in surface waters. At Tooth Lake there were no tailings in the lake but surface waters contained arsenic up to 600 µg/L in the surface waters. Adjacent to the lake large amounts of waste rock are found. Further research would be needed to demonstrate how much waste rock contributes to arsenic in surface waters. A detailed and extensive survey is also necessary to accurately determine the extent of tailings migration and contamination throughout the Cobalt area.

4.5 Conclusion

This study has provided new and important data from lakes in the Cobalt and Silver Center mining areas. Many of these lakes having been investigated for the first time in this study. Not surprisingly, this resulted in the identification of many lakes that, prior to this study, were thought to be in a pristine state, but are now known to be contaminated from the nearby mining activity. This study has shown that arsenic contamination throughout the region in areas influenced by early mining activity is severe and widespread throughout the water network. The probable effect levels for the protection of

aquatic life for arsenic in sediment and surface waters was exceeded by as much as 635 times the objective (17 mg/kg; CCME, 1999) and 194 times the objective (5 µg/L; CCME, 2001), respectively. Many of these lakes are either, near the Town of Cobalt, or drain into the nearby Lake Temiskaming, which is a recreational centre and headwater for the Ottawa River. Our study was primarily concerned with investigating background conditions and conclusively determined that the Cobalt region possesses a naturally elevated geochemical background that is due to the unique, large, and extensive silver-arsenide (Cobalt-type) deposits in the region. From control lakes, the natural variation of background arsenic concentrations was determined to be as high as 14 mg/kg, more than double that from the nearby Gowganda and Temagami regions (<6 mg/kg). However, these determinations were from un-exploited areas that likely lack any significant mineralization. In some locations, un-exploited areas with comparatively less mineral potential than Cobalt, naturally anomalous arsenic were found to be as high as 97 mg/kg from the Gowganda and Temagami regions. With this in mind, and the fact that Cobalt, ON, boasted some of the richest silver deposits in the world, then the background values (100-200 mg/kg) obtained below tailings from contaminated lakes in Cobalt and Silver Center may be reasonable estimates of natural background for this region. Regardless of a true background value, arsenic rich legacy tailings such as those found around Cobalt, ON, are an issue over much of the world and they present unique challenges for management and remediation.

4.6 References

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Figure 4.1: Geological, Hydrological Map for the Cobalt Area. The sample ID box shows the relative arsenic concentration in surface waters. Insets show location of remote sampling locations. Lake codes correspond to lake names in Table 4.3.

Table 4.1: Location of sampling sites (UTM zone 17N), and surface water arsenic concentration ($\mu\text{g/L}$) and lake classification. The classification contaminated* denotes lakes that have been impacted by tailings migration.

Lake Name	Easting	Northing	Arsenic	Classification
Brady Lake	602066	5246128	140	contaminated
Cart Lake	599346	5248521	972	contaminated
Cobalt Lake	599038	5249383	495	contaminated
Crosswise Lake	602580	5248800	82.4	contaminated
Fourclaim Lake	612635	5228145	542	contaminated
Kerr Lake	601519	5247958	348	contaminated
N. Peterson Lake	600245	5249126	312	contaminated
S. Peterson Lake	600663	5248931	297	contaminated
Tooth Lake	612959	5226728	635	contaminated
Ibsen Pond	601702	5245073	142	contaminated*
Kirk Lake #1	603664	5246742	34	contaminated*
Kirk Lake #2	603510	5247013	32.6	contaminated*
Kirk Lake #3	603823	5246562	79.8	contaminated*
Maidens Lake	614885	5228640	23.6	contaminated*
New Lake Middle	601139	5244333	36.8	contaminated*
New Lake North	601254	5244965	36.6	contaminated*
Clear Lake	597127	5249785	2	uncontaminated
Frog Lake	601742	5242455	0.7	uncontaminated
Goodwin Lake	608945	5242693	1.4	uncontaminated
Green Lake	597093	5248897	2.9	uncontaminated
Ice Chisel Lake	599108	5240629	1.7	uncontaminated
Mary Ann Lake	602659	5242849	0.9	uncontaminated
Nichol Lake	605881	5244401	0.7	uncontaminated
N. Pickerel Lake	597459	5246724	5	uncontaminated
Oxbow Lake	614038	5225707	0.7	uncontaminated
Pine Lake East	605697	5235453	2.05	uncontaminated
Pine Lake West	604042	5235854	0.4	uncontaminated
Silver Lake	602930	5243810	7.3	uncontaminated
S. Pickerel Lake	597618	5246053	3.3	uncontaminated

Figure 4.2: Box plots of arsenic concentrations in surface waters using all sampled lakes, and using sub-datasets of only control lakes, contaminated lakes, and lakes influenced by tailings migration. The red addition symbol is the mean value.

Figure 4.3: Bi-plot of principal component 1 and 2 of the PCA conducted on surface waters that were CLR transformed. The black, green and red ellipses are a 95% confidence interval for data containing contaminated, migration, and control lakes, respectively.

Table 4.2: Component loadings for PCA conducted on clr-transformed surface waters geochemical data.

Parameter	PC1	PC2
Bicarbonate	-0.1319	0.795708
Chloride	0.152487	0.619529
Sulphate	-0.52578	0.453744
Calcium	-0.10994	0.801129
Magnesium	-0.07419	0.728565
Sodium	0.152878	0.655751
Potassium	-0.27602	0.237945
Aluminum	0.992914	-0.03884
Antimony	-0.9304	-0.26525
Arsenic	-0.83845	-0.398
Cadmium	0.674577	-0.30414
Cobalt	-0.58064	-0.60225
Copper	0.118713	-0.49123
Iron	0.822382	-0.18091
Lead	0.780127	-0.42288
Molybdenum	-0.8462	-0.37943
Nickel	-0.63142	-0.61099
Silver	0.66233	-0.02189
Uranium	0.40167	-0.52172
Zinc	0.618231	-0.4459
% of Variance	30.3	21.2
Cumulative Variance	30.3	51.5

Figure 4.4: log-log transformed surface water vs surface sediment.

S. Peterson Lake

Ibsen Pond

Cart Lake

Cobalt Lake

N. Peterson Lake

Brady Lake

Crosswise Lake

New Lake + Maidens Lake

Fourclain Lake

Figure 4.5: Core profiles for arsenic in contaminated lakes and arsenic in surface waters. Each figure contains a schematic of its core. For the core schematics grey=tailings material, brown=lake sediment, brown with grey spots=mixed tailings and lake sediment, grey with horizontal lines = varves. The horizontal scales are not identical between graphs. The upper scale is for the blue dot, which indicates the concentration of arsenic in surface water. The bottom horizontal scale is arsenic in lake sediment.

Table 4.3: Geochemical (mg/kg) and Loss on Ignition (Water and Organic Content) Data for Lake Sediment in Control and Contaminated lakes. Catchment Geology codes: Arch= Archean Volcanics/Sediments, Gow=Gowganda Formation, Gr=Granite, Np=Nipissing, Lr=Lorrain Formation.

Lake Name (Map Code)	Catchment Geology	Depth (cm)	As	Sb	Co	Ni	Ag	Water content (%wet)	Organic Content (%dry)
Clear (CLR)	Arch	1	11	0.5	12	39	0.2	58.7	7.42
		4	12.3	0.5	8	37	0.2	81.12	24.4
		20	37	2.2	26	61	5.1	78.14	20.58
		38	0.5	0.5	6	33	0.2	76.85	20.77
Green (GRN)	Arch	0-5	109	3.8	27	63	3.3	97.8	54.79
		20	1.8	0.5	6	22	0.2	94.56	61.76
		72	1.8	0.5	6	25	0.2	94.07	61.41
N. Pickerel (N-Pick.L)	Gow Arch	0-3.5	27	0.9	5	29	1.3	89.75	25.16
		5.5	19	0.7	3	25	0.4	75.09	13.05
		20	11.2	0.5	2	19	0.2	91.58	56.21
		62	12	0.5	4	24	0.2	92.72	49.5
S. Pickerel (S-Pick.L)	Gow Arch	0-3	48	2	11	60	1.1	98.8	80.58
		20	10	0.5	3	14	0.2	95.91	60.66
		63	12	0.5	3	24	0.2	95.65	68.65
Nichol (Nic.L)	Gr Np Lr	0-1	12.8	1	6	46	0.9	98.4	62.64
		1-3	15	1.1	7	31	0.8	97.49	65.01
		20	1	0.5	2	16	0.2	96.45	70.28
		54	0.8	0.5	2	13	0.2	96.97	89.94
Silver (Silv.L)	Gr Np Arch	0-4	23	0.7	10	40	1.1	98.61	77.38
		20	1.4	0.5	4	21	0.2	97.41	69.27
		55	9	0.5	12	23	1.2	93.65	68.74
Goodwin (GW)	Gr Np Lr	0-3	9.5	0.8	11	41	0.7	92.11	63.57
		5	2.6	0.5	7	22	0.2	91.34	37.76
		20	1.2	0.5	7	24	0.2	88.98	38.72
		25	2	0.5	7	25	0.2	88.98	39.68
Mary Anne (MA)	Np	0-5	13	1.7	9	49	1.1	97.12	67.2
		20	1.4	0.5	4	28	0.2	94.56	59.19
		40	1.8	0.5	6	28	0.2	93.26	55.31
Frog (FL)	Np	0-3	10.4	0.8	65	34	1.7	88.45	49.09
		5	6.8	0.5	59	27	1.7	90.11	51.47
		20	5.6	0.5	76	31	1.5	90.46	57.56
		50	7.8	0.5	87	32	1.5	87.79	54.33
Ice Chisel (ICL)	Gow Np	0-1	3.2	0.5	8	30	0.2	96.73	48.06
		5.5	2.2	0.5	9	31	3.5	91.15	39.62
		10.5	4.1	0.5	7	24	5.3	89.15	47.22

Table 4.3: Continued.

Lake Name (Map Code)	Catchment Geology	Depth (cm)	As	Sb	Co	Ni	Ag	Water content (%wet)	Organic Content (%dry)
E. Pine (PLE)	Gr Np Lr Arch	0-3	3.9	0.5	3	23	0.2	89.92	71.61
		5	1.2	0.7	1	11	0.2	90.12	24.32
		20	0.5	0.5	1	6	0.2	75.48	75.48
		28	0.5	0.5	1	8	0.2	78.75	78.75
W. Pine (WPL)	Gr Np Lr Arch	0-3	12	1	12	33	2.8	92.03	38.63
		5	6.4	0.5	9	30	0.9	91.24	38.09
		20	3.7	0.5	9	33	0.4	90.08	37.37
		34	4.2	0.5	10	33	0.4	89.77	51.76
Oxbow (OXL)	Gow Np Arch	0-5	12.4	0.8	12	56	0.4	97.8	76.16
		20	6.6	0.5	12	33	0.2	97.96	76.32
		32	6.9	0.5	16	34	0.2	96.65	79.01
Cobalt (CoL)	Gow Arch	0-3	10800	97.5	2070	719	109	59.16	95.18
		5	8050	71.9	1710	635	99	43.15	3.67
		10	1090	34.5	498	252	41.9	22.17	1.64
Cart (CartL)	Gow Np Arch	0-3	4510	31.1	623	259	51	90.9	24.26
		9	965	35.5	327	234	39.6	51.39	4.65
		13	1310	48.3	341	224	32.6	57.04	6.21
		19	915	20.1	204	145	47.7	90.25	51.23
		30	169	6.1	54	43	3.5	95.33	92.28
		45	1650	52.8	393	257	38	96.25	79.36
		60	522	24.4	145	90	13.9	95.87	90.5
N. Peterson (NPL)	Gow Np Arch	0-5	2650	105	569	1860	189	90.76	19.57
		20	335	8.8	70	149	11.6	95.93	57.96
		38	134	6.2	36	49	1.7	94.95	67.93
S. Peterson (SPL)	Gow Np Arch	0-2	2440	51.8	730	437	225	81.88	0.29
		4	3290	88.5	708	408	265	87.26	0.61
		14	1560	52.3	465	226	285	54.4	0.21
		24	2050	79	431	240	206	88.11	0.67
		41	172	4	36	39	1.5	93.54	59.97
		59	177	3.8	42	43	0.9	93.16	70.27
		63	234	8.3	53	48	8.1	93.78	68.21
Kerr (KL)	Gow Np Arch	0-1	702	12.9	583	145	10.8	60.85	13.87
		3	185	6.3	121	38	2.5	49.88	8.3
		6	80	2.6	54	22	1.1	34.84	4.93
Brady (BL)	Np Arch	0-3	1950	85.3	387	108	71.8	92.85	23.54
		5	470	15.4	57	31	10.6	96.31	62.81
		20	13	0.8	8	19	0.7	95.19	70.39
		40	4.8	0.5	10	17	0.3	96.41	96.41

Table 4.3: Continued.

Lake Name (Map Code)	Catchment Geology	Depth (cm)	As	Sb	Co	Ni	Ag	Water content (%wet)	Organic Content (%dry)
Crosswise (CWL)	Np Arch	0-2	1020	32.15	408	996	88.8	67.07	6.31
		5	609	32.95	130	167	91	79.95	13.69
		20	4.4	0.5	7	41	0.2	79.55	15.78
		36	8.7	0.5	20	55	0.6	77.25	16.32
Kirk 1 (Krk-1)	Gr Arch	0-3	1160	41.2	458	197	90.3	75.81	8.44
		20	44	2.1	34	50	3.4	78.93	19.42
		29	43	2.5	32	49	3.8	87.94	30.46
Kirk 2 (Krk-2)	Gr Arch	0-2	3630	58.3	823	378	102	58.41	6.76
		20	1240	64.7	365	224	130	37.42	2.98
		29	1160	56.3	325	209	121	43.96	4.33
		31	260	16.5	64	61	22	86.42	32.45
Kirk 3 (Krk-3)	Gr Arch	0-2	2180	63.1	500	175	93.2	67.35	8.26
		18	381	17.9	106	78	29.4	78.54	21.92
Ibsen Pond (IBP)	Arch	0-1	3490	14.8	961	160	59.1	92.7	43.14
		9	1840	18.6	515	117	69.1	91.81	36.76
		12	936	27	337	133	102	88.4	25.06
		14	950	33.3	308	146	109	81.02	16.15
		15	1340	43.4	383	192	122	79.88	15
		16	1440	46.6	389	204	127	61.51	6.19
		17	1450	44.8	383	198	129	58.86	5.2
		19	653	16.4	191	92	43.5	86.3	23.57
		30	315	2.4	101	59	26.8	94.09	70.84
		38	122	10.3	50	39	11.1	95.52	68.32
N. New (NLN)	Arch	0-3	236	11.8	64	91	10.8	96.22	71.67
		4	260	21.7	91	89	25.1	95.2	62.05
		20	33	2.4	16	34	2.8	96.23	79.5
		39	9.6	0.5	9	27	1.2	95.43	73.26

Table 4.3: Continued.

Lake Name (Map Code)	Catchment Geology	Depth (cm)	As	Sb	Co	Ni	Ag	Water content (%wet)	Organic Content (%dry)
Middle New (NLM)	Arch	0-5	492	13.1	107	56	10.4	98.02	55.06
		20	131	2.4	80	33	3.3	95.18	64.64
		57	11.1	0.4	12	28	1.8	92.98	58.13
Fourclaim (FCL)	Gow Arch	0-3	7420	55.7	1510	669	181	88.72	19.74
		5	5380	56.4	1180	524	140	94.84	26
		25	64	1.1	10	32	1.2	97.04	71.97
		48	83	1	12	35	1.2	95.73	69
Maidens (MDL)	Gow Lr Np	0-4	185	6	56	3	2.6	95.35	45.73
		7	59	1.7	22	2	0.9	96.31	42.19
		19	9.3	0.5	12	4	0.4	91.33	25.58
		33	1.7	0.5	8	2	0.2	91.67	27.08
		41	4.4	0.5	13	8	0.3	83.58	18.33
Tooth 1 (TL-1)	Gow/Np/Arch	0-1	140	0.5	9	17	0.3	35.72	2.15
		3	37	0.5	17	37	0.2	45.63	2.76
		4	13.3	0.5	25	61	0.2	51.3	3.18
		20	3.8	0.5	23	59	0.2	52.04	2.12
		50	2.6	0.5	22	62	0.2	44.52	3.04
Tooth 2 (TL-2)	Gow/Np/Arch	1	34	0.5	6	11	0.2	39.34	1.94
		2	27	0.5	10	21	0.2	39.43	2
		4	13	0.5	27	62	0.3	37.99	1.57
		18	8.1	0.5	25	61	0.2	48.61	2.63

4.6a

4.6b

Figure 4.6 a,b: Histogram (a) and CF-Curve (b) of samples from contaminated lakes in Cobalt.

Figure 4.7: Average plot of Arsenic, Antimony, Cobalt, Nickel, and Silver in Control Lakes.

Figure 4.8: Average plot of Organic (%dry weight) and Water (%wet weight) content for Control Lakes.

4.9a

4.9b

Figure 4.9a,b: Histogram (a) and CF-Curve (b) of samples from Control Lakes in Cobalt. The red dotted line indicates the 17 mg/kg objective for the protection of aquatic life.

Figure 4.10: Bi-plot of PC1 (44%) and PC2 (21%) of PCA conducted on lake sediment geochemistry that was clr-transformed. The red ellipse is the 95% confidence interval for data containing control lakes.

Table 4.4: PCA loadings of clr-transformed geochemical sediment data from Cobalt, ON.

Parameter	PC1	PC2
Arsenic	1.445123	-0.12611
Barium	-1.44995	0.088242
Beryllium	-1.3092	-0.34786
Bismuth	-0.09854	0.083699
Boron	-1.24779	0.700147
Cadmium	1.108893	0.618783
Chromium	-0.95725	-0.98313
Cobalt	1.351157	-0.50293
Copper	0.223082	0.773245
Iron	-0.48424	-1.36557
Lead	1.218483	0.181902
Manganese	-0.64148	-0.93222
Molybdenum	-0.6154	0.865075
Nickel	0.440217	-0.34251
Selenium	-1.23369	0.851465
Silver	1.47763	-0.04618
Thallium	-1.42909	0.268291
Titanium	-0.78029	-1.2223
Uranium	-1.31064	0.494803
Vanadium	-0.34315	-1.29635
Zinc	-0.56148	0.76466
% of Variance	44.14	21.92
Cumulative Variance	44.14	66.06

4.11a

4.11b

Figure 4.11a,b; Histogram (a) and CF-Curve (b) of lake sediment from the Gowganda and Temagami Superior province from catchments that have the same rock types from the Gowganda area.

Chapter 5:

Conclusions

This thesis investigates lake sediment geochemistry from regions in Northeastern Ontario from the areas around Gowganda, Temagami, Cobalt and Silver Center. The environmental legacy of the Cobalt mining camp represents an area that has been extremely impacted by arsenic-rich mine waste. The primary objectives of this thesis were to determine the magnitude and spatial extent of arsenic contamination in Cobalt, ON, and to investigate realistic background concentrations of arsenic for the region.

To aid in this investigation in Chapter 3 the adjacent areas of Temagami and Gowganda were investigated using historical lake sediment records collected by the Ontario Geological Survey (OGS) (Hamilton, 1997; Takats and Dyer, 2004). This was done to determine background and anomalous geochemical and arsenic concentrations over a much larger spatial scale in an effort to establish the controlling factors influencing lake sediment geochemistry, under similar geological, biological, and climatic conditions. This chapter highlighted that bedrock geology is an important control on lake sediment geochemistry and that specific geochemical assemblages can be spatially associated to specific bedrock types. I tested the effectiveness of a random forest classifier in its ability to identify the catchment properties of a sample in terms of geologic province and bedrock geology based on its sediment geochemistry. The results of this test were promising, especially in regional terms, as a 6% out of bag error was achieved for correctly identifying geological provinces. At the more local scale, a 36% out of bag error rate was achieved for identifying the samples catchment bedrock geology. Misclassified results show the impacts of mixing between co-occurring rock types in catchments and

highlight that some rock types are geochemically dominant compared to others. Finally, mapping PC scores indicated that large amounts of variance within the dataset could be attributed to geologic parameters on local and regional scales specifically highlighting that substantial differences existed in lake sediment geochemistry between geologic provinces, rock types, and that interactions between rock types can produce distinct geochemical assemblages. The PCA was highly efficient at highlighting areas favourable for Cobalt-type mineralization, showing positive loadings for the Cobalt-type indicator elements and being spatially related to favourable geological conditions for that deposit type as well as known mineral deposits in the Mineral Deposit Index database. The research in this chapter can also be valuable for environmental purposes as it provides evidence of the natural variability in background lake sediment geochemistry, which can change dramatically depending on geological properties of the area in question. In legacy mining sites where background sedimentary geochemical data were not obtained prior to mining, studies such as these can help provide realistic restoration targets that are targeted to the geological setting of the lake.

In Chapter 4 the current contaminant levels in lake sediments and surface waters in Cobalt and Silver Center mining camps were determined. In contaminated lakes, mine tailings on the lake bottom were found to contain up to 10,800 mg/kg of arsenic, which is 635 times the objective for the protection of aquatic life and 981 times the mean value found in control lakes (11 mg/kg). However, tailings in contaminated lakes were typically in the 1000 - 3000 mg/kg range. Surface waters in contaminated lakes also contained extremely alarming amounts of arsenic, up to 972 µg/L which is 97 times the drinking water standard of 10 µg/L and 194 times the 5 µg/L objective for the protection of

aquatic life. The mean arsenic concentration in contaminated lakes was substantially lower (431 mg/kg) but still 86 times the 5 µg/L objective for the protection of aquatic life and 195 times the mean arsenic in surface waters of control lakes (2.2 µg/L) . Three methods for determining background arsenic concentrations were applied using control lakes from Cobalt, data from Chapter 3, and sampling below tailings in contaminated lakes. In the PCA conducted on lake sediment, some samples obtained below tailings in contaminated lakes fell within the 95% confidence interval ellipse for control lakes, indicating that these samples may reflect natural background conditions, even though arsenic was found to be up to 187 mg/kg. A reasonably flexible background range of 100-200 mg/kg was determined based on data from the 3 approaches. The study also showed that on-going tailings migration and surface waters flowing from contaminated catchments can substantially impact lakes downstream that had no mining activity in their watershed. In some lakes, arsenic in surface sediments was found to be up to 490 mg/kg, more than 35 times the maximum background range from control lakes (14 mg/kg), even though no evidence of physical tailings were found. It was also found that natural recovery of these contaminated lakes is highly unlikely because the redox profile of lake sediment causes arsenic concentrations to remain highest at the water sediment interface, even if tailings are buried. This process prevents any recovery of the sediment biological community that dwell in the upper sediment. This study has shown that arsenic contamination throughout the region in areas influenced by early mining activity is severe and widespread throughout the water network. It presented new data on many lakes that had never been sampled before and identified some lakes that were thought to be pristine, but are now known to contain alarmingly high arsenic concentrations. This research is

important because it showed that arsenic concentrations are naturally elevated in this region, and are substantially above regulatory objectives. Because the background was found to be so high, it may be an incentive for industrial or government organizations to initiate remediation efforts in the area.

Future work in the Cobalt area could focus on obtaining more background samples to better constrain the natural range of background variation in the contaminated regions. Deeper sediment cores obtained from South and North Peterson Lake, Cart Lake, Fourclaim Lake, Ibsen Pond, and Kirk Lake may represent good targets for this. Also, given the widespread nature of contamination throughout the region a detailed and systematic survey is needed to identify all of the mine waste and affected areas. Some locations in this study indicated that waste rock may be a significant contributor to arsenic in surface waters, so research could be conducted to determine the relative contributions of arsenic from tailings and waste rock to local surface waters; which could benefit remediation strategies. A detailed investigation of the redox conditions at the water sediment interface would also provide useful information to remediation strategies. This would help identify whether Mn-Fe oxides at the water sediment interface are preventing or allowing arsenic sourced from submerged tailings being a source of arsenic to surface waters.

In summary, this thesis provides empirical evidence on background conditions in lake sediment that has implications for realistic restoration targets sites impacted by legacy mine contamination. Arsenic concentrations can vary widely in nature and if restoration is to take place it is important that restoration targets are based on the best available scientific evidence for that region. These results can help inform management

and restoration plans for a region that has been heavily impacted by legacy arsenic contamination.

Appendix A – CF-curves from Temagami and Gowganda

Sheet 1: CF-curves from Temagami and Gowganda, Superior watersheds

Sheet 2: CF-curves from Gowganda and Temagami; Grenville watersheds

Sheet 3: CF-curves from Temagami and Gowganda; All watersheds in both provinces

Sheet 4: CF-curves from Temagami and Gowganda; Nipissing Diabase watersheds

Sheet 5: CF-curves from Temagami and Gowganda; Gowganda formation watersheds

Sheet 6: CF-curves from Temagami and Gowganda; Lorrain formation watersheds

Sheet 7: CF-curves from Temagami and Gowganda; Granite watersheds

Sheet 8: CF-curves from Temagami and Gowganda; Gabbro/Ultramafic watersheds

Sheet 9: CF-curves from Temagami and Gowganda; Archean Sedimentary watersheds

Sheet 10: CF-curves from Temagami and Gowganda; Archean Felsic/Intermediate watersheds

Sheet 11: CF-curves from Temagami and Gowganda; Archean Mafic/Intermediate watersheds

Sheet 12: CF-curves from Temagami and Gowganda; Para-Gneiss watersheds

Sheet 13: CF-curves from Temagami and Gowganda; Biotite Gneiss/migmatite watersheds

Sheet 14: CF-curves from Temagami and Gowganda; Anorthosite/Gabbro watersheds

Sheet 15: CF-curves from Temagami and Gowganda Tonalite/Granodiorite watersheds

Sheet 16: CF-curves from Gowganda, Nipissing Diabase – Gowganda – Lorrain watersheds

Sheet 17: CF-curves from Gowganda, Nipissing Diabase – Gowganda – Lorrain – Granite watersheds

Sheet 18: CF-curves from Gowganda, Superior province – All watersheds

Sheet 19: CF-curves from Gowganda, Nipissing Diabase watersheds

Sheet 20: CF-curves from Gowganda, Gowganda Formation watersheds

Sheet 21: CF-curves from Gowganda, Lorrain Formation watersheds

Sheet 22: CF-curves from Gowganda, Granite watersheds

Sheet 23: CF-curves from Gowganda, Gabbro/Ultramafic watersheds

Sheet 24: CF-curves from Gowganda, Archean Sedimentary watersheds

Sheet 25: CF-curves from Archean Felsic/Intermediate watersheds

Sheet 26: CF-curves from Archean Mafic/Intermediate volcanic watersheds

Sheet 27: CF-curves from Temagami, All watersheds (Superior and Grenville Provinces)

Sheet 28: CF-curves from Temagami, Nipissing – Gowganda – Lorrain watersheds

Sheet 29: CF-curves from Temagami, Nipissing – Granite watersheds

Sheet 30: CF-curves from Temagami, Nipissing – Gowganda – Granite

Sheet 31: CF-curves from Temagami, Superior Province watersheds

Sheet 32: CF-curves from Temagami, Archean Mafic/Intermediate Volcanic watersheds

Sheet 33: CF-curves from Temagami, Archean Felsic/Intermediate Volcanics watersheds

Sheet 34: CF-curves from Temagami, Archean Sedimentary watersheds

Sheet 35: CF-curves from Temagami, Gabbro/Ultramafic watersheds

Sheet 36: CF-curves from Temagami, Granite watersheds

Sheet 37: CF-curves from Temagami, Lorrain Formation watersheds

Sheet 38: CF-curves from Temagami, Gowganda Formation watersheds

Sheet 39: CF-curves from Temagami, Nipissing Diabase watersheds

Sheet 40: CF-curves from Temagami, Grenville Front Tectonic Zone watersheds

Appendix B: Supplementary Principal Component Maps

Temagami - principal component 4

Figure B-1: Principal Component 4 Map for the Temagami region. The high and low values correspond to the interpolated principal component scores for all the samples after a clr transform was conducted on the raw geochemical data. The light grey lines are the geologic boundaries of the rock units shown in Figure 1. The total variance explained by principal component 4 is 7.29%. The hollow diamonds and crossed hammer symbols indicate mineral occurrences and mineral deposits, respectively.

Gowganda - principal component 3

Figure B-2: Principal Component 3 Map for the Gowganda region. The high and low values correspond to the interpolated principal component scores for all the samples after a clr transform was conducted on the raw geochemical data. The light grey lines are the geologic boundaries of the rock units shown in Figure 1. The total variance explained by principal component 3 is 11.43%. The hollow diamonds and crossed hammer symbols indicate mineral occurrences and mineral deposits, respectively.

Gowganda - principal component 4

Figure B-3: Principal Component 4 Map for the Gowganda region. The high and low values correspond to the interpolated principal component scores for all the samples after a clr transform was conducted on the raw geochemical data. The light grey lines are the geologic boundaries of the rock units shown in Figure 1. The total variance explained by principal component 4 is 6.96%. The hollow diamonds and crossed hammer symbols indicate mineral occurrences and mineral deposits, respectively.

Gowganda - principal component 5

Figure B-4: Principal Component 5 Map for the Gowganda region. The high and low values correspond to the interpolated principal component scores for all the samples after a clr transform was conducted on the raw geochemical data. The light grey lines are the geologic boundaries of the rock units shown in Figure 1. The total variance explained by principal component 4 is 4.04%. The hollow diamonds and crossed hammer symbols indicate mineral occurrences and mineral deposits, respectively.

Appendix C: Supplementary Maps

Figure C-1: Map showing location of Cobalt, Silver center, Gowganda and Temagami in Ontario. The grey area shows the limits of the Ontario Geological Survey lake sediment surveys from Temagami and Gowganda.

Figure C-2: Sampling locations (red dots) from the lake sediment surveys by the Ontario Geological Survey in the Gowganda (upper left) and Temagami (bottom Right) regions.

Figure C-3: Sampling locations (red dots) from the lake sediment surveys by the Ontario Geological Survey in the Gowganda (upper left) and Temagami (bottom Right) regions. Sampling locations from the Cobalt sampling program (black dots). The area within the red outline shows the approximate drainage area for the Montreal River. Outside this area, drainage flows toward Lake Temiskaming.

Figure C-4: Sample locations (black dots) with their map code, mine tailings (grey), lakes and streams (blue), wetlands (yellow with horizontal lines), and city limits (pale yellow), past producing mines (crossed hammers), and mineral occurrences (hollow diamond) in the Cobalt area. Arrows show the drainage directions.

Figure C-5: Sample locations (black dots) with their map code, mine tailings (grey), lakes and streams (blue), wetlands (yellow with horizontal lines), and city limits (pale yellow), past producing mines (crossed hammers), and mineral occurrences (hollow diamond) in the Silver Center area. Arrows show the drainage directions.

Figure C-6: Elemental map of antimony concentrations (mg/kg) in lake sediment in the Temagami region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-7: Elemental map of arsenic concentrations (mg/kg) in lake sediment in the Temagami region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-8: Elemental map of cobalt concentrations (mg/kg) in lake sediment in the Temagami region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-9: Elemental map of copper concentrations (mg/kg) in lake sediment in the Temagami region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-10: Elemental map of nickel concentrations (mg/kg) in lake sediment in the Temagami region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-11: Elemental map of silver concentrations (mg/kg) in lake sediment in the Temagami region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-12: Elemental map of antimony concentrations (mg/kg) in lake sediment in the Gowganda region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-13: Elemental map of arsenic concentrations (mg/kg) in lake sediment in the Gowganda region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-14: Elemental map of cobalt concentrations (mg/kg) in lake sediment in the Gowganda region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-15: Elemental map of copper concentrations (mg/kg) in lake sediment in the Gowganda region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-16: Elemental map of nickel concentrations (mg/kg) in lake sediment in the Gowganda region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Figure C-17: Elemental map of silver concentrations (mg/kg) in lake sediment in the Gowganda region. Interpolation done using empirical bayesian kriging in ArcGIS 10.3.1. Grid shows the geographic townships.

Appendix D: Supplementary Tables

Table D-1: YSI measurements from lakes in the Cobalt and Silver Center regions. UTM zone is 17N.

Lake Name	Easting	Northing	Depth (m)	Temperature	Conductivity	DO%	pH	ORP
Frog Lake	601742	5242455	0	19.3	110.2	142.5	6.84	231.5
			1	18.9	108	127.2	6.87	232.7
			2	13.3	81.8	154.6	6.91	234.1
			3	8.4	87.5	173.2	6.7	235.7
			4	5.7	95	140	6.5	235
			5	4.6	95.3	90	6.5	232
			6	4	96	72	6.52	229.4
			7	3.9	98	66	6.54	227.5
			8	3.9	98	43	6.64	225.8
			9	3.9	104	51	7.15	224
			10	3.8	126.6	49	9.1	224.3
Clear Lake	597127	5249785	0	19.4	228	224	8.05	234
			1	19.2	226	209	8.05	233
			2	19	225.9	209	8.02	233.5
			3	18	217	207	8.03	234
			4	12.4	205	258	8	235.4
			5	8.1	192.5	291	7.85	236.6
			6	6.1	185.6	288	7.75	236.6
			7	5.3	182.7	254	7.68	235.3
			8	4.7	181	225	7.68	233.9
Green Lake	597093	5248897	0	21.7	182.5	226	8.47	231.4
			1	19.1	169	247	8.3	231
			2	13	196	286	8.05	235.7
			3	7.1	240	313	9.65	234.9
			4	7.2	283	260	10.04	231
			5	7	240	207	9.7	224.7
North Pickerel Lake	597459	5246724	0	0.1	100	15	7.65	151
			1	3	178.9	27	7.83	99.5
			1.5	4.7	204.1	3	6.75	-75
South Pickerel Lake	597618	5246053	0	0.1	209.9	17	7.5	175.2
			1	2.6	181.7	20	7.37	163.8
			2	4.2	185.9	4	7.15	166
			2.5	4.8	228.5	2	6.71	-106.9

Table D-1: Continued

Lake Name	Easting	Northing	Depth (m)	Temperature	Conductivity	DO%	pH	ORP
S. Peterson Lake	600663	5248931	0	19.8	193	194	8.32	223.9
			1	19.8	192.8	202	8.33	223.9
			2	19.7	192.7	195.3	8.31	223.8
			3	19.6	195.2	191.6	8.31	223.9
			4	15.4	197	236.4	8.18	228
			5	9.1	184.6	317	8.02	229
			6	9	185.2	263	9.04	228.3
N. Peterson Lake	600245	5249126	0	19.4	196	275	7.97	227.7
			1	19.4	197.3	234	8	228.1
			2	19.4	196.5	237	8.14	228.3
Kerr Lake	601519	5247958	0	19.2	284	274	8.95	231
			1	19.1	283	241	8.85	231
			2	19	282	222	8.77	231.3
			3	18.9	277	215	8.66	233.1
			4	9.4	252	304	8.48	235.3
			5	6.3	230	322	8.43	235.2
			6	5.2	223	134	8.43	234
Fourclaim Lake	612635	5228145	0	23.1	94.9	264	8.9	231.6
			1	22.9	93.6	182	8.82	233
			2	22	93	186	8.79	229.5
			3	21.8	92	178	8.75	229
			4	15.7	98.2	198	8.5	230
Oxbow Lake	614038	5225707	0	20.4	23.6	150	8.28	228.7
			1	20.3	23.5	114	8.14	228.2
			2	19.7	73.9	86	9.37	226.4
Ice Chisel Lake	599108	5240629	0	0.01	9.7	115	5.6	240
			1	2.5	8	65	4.8	252
			2	4	8.2	52	4.7	260
			3	4.2	8.9	17	4.72	260
			4	4.5	11.8	2	5.3	30
			5	4.5	10	3	5.42	-15
			6	4.5	10.6	2	5.53	-21

Table D-1: Continued

Lake Name	Easting	Northing	Depth (m)	Temperature	Conductivity	DO%	pH	ORP
Maidens Lake	614885	5228640	0	21.5	103	226	8.36	225
			1	21.5	102.9	207	8.31	223.9
			2	21.3	102	205	8.31	223.7
			3	20.9	101	199	8.31	223.2
			4	19.1	98.8	210	8.33	223
			5	10.4	95.7	284	8.2	226.4
			6	9.5	95.3	277	8.08	226
			7	7.5	95.7	268	8.14	225.6
			8	6.8	95.8	258	8.25	224
			9	6.6	96.1	246	8.7	225
			10	6.7	98.5	246	10.07	220.4
Cart Lake	599346	5248521	0	0.2	339	6	7.5	-70.6
			1	1.7	339	3	7.35	-85.4
			1.5	1.8	347.2	3	7.21	-96.5
			2	1.8	343.8	3	7.17	-100.7
Tooth Lake	612959	5226728	0	22	65	208	8.78	227.2
			1	22	65	184	8.7	226.2
			2	21.6	64.1	177	8.63	226.2
			3	21.4	64	169	8.63	225
			4	21	63	168	8.64	225
			5	20.9	61	170	8.66	225
			6	16.4	55	207	8.67	225.9
			7	12.4	52	131	8.64	225
			8	10	47	144	8.61	276
Silver Lake	602930	5243810	0	21	113.7	95	8.19	219
Ibsen Pond	601702	5245073	0	21.4	133.8	102.3	8.42	219
			1	20.3	129	118.7	8.55	218
			2	18.8	144.8	90.9	7.9	222.9
			3	13.5	163.1	90.4	7.67	224.6
			4	10	175.2	86	9.82	224.9
			5	9.7	201	55	10.55	223.1
Crosswise Lake	602580	5248800	0	21.8	129	108.8	8.13	221
			1	21.8	129	107	8.08	221
			2	21.8	129.3	104	8.05	221
			3	21.7	129	100	8.06	220.7
			4	21.6	125	101.6	7.99	221
			5	18	116.1	108.4	7.87	220.4
			6	13.1	108	90	7.71	225
			7	11.3	108.9	88.2	9.5	225

Table D-1: Continued

Lake Name	Easting	Northing	Depth (m)	Temperature	Conductivity	DO%	pH	ORP
New Lake Middle	601139	5244333	0	21.9	86.7	128	8.21	220.9
			1	21.4	85.7	116	8.21	221.2
			2	21	84.7	113.9	8.22	221.5
			3	20	83.4	110	8.16	220.7
			4	13.3	77.6	129	7.96	225.6
			5	9	76.2	127.1	7.79	226
			6	6	74.8	129.1	7.76	226
			7	5.4	74.4	90.1	7.81	224
			8	4.8	74.3	82	7.88	229
			9	4.5	74.5	72.8	7.98	220.5
New Lake North	601254	5244965	0	22.9	88.6	98.6	8.21	220.4
			1	22.8	88.3	96	8.19	220.6
			2	22.7	88.3	93	8.16	221
			3	20.7	101.3	76	10.73	220
Cobalt Lake (Winter)	599038	5249383	0	0.2	294.6	25	7.8	191.3
			1	1.7	390	25	7.73	183.4
			2	3.1	393	54	7.71	144.4
			3	3.5	395.3	56	7.63	143.3
			4	3.7	397.2	50	7.56	147.6
			5	4.1	399.8	26	7.47	148.5
			6	4.3	408.1	7	7.39	130
			7	4.5	354.6	2	7.55	-169.9
Cobalt Lake (Summer)	599038	5249383	0	22	325	106.7	8.35	219
			1	21.8	324	104.6	8.36	219
			2	21.6	324	104	8.37	219
			3	8.4	401	104	8.36	225
			4	6.7	378	138	7.93	226
			5	5.7	369	118.5	7.88	223
			6	5.5	367.5	105	7.83	222.1
			7	5.5	367.8	94.2	7.88	217
Goodwin Lake	608945	5242693	0	22	140.8	114.7	8.13	221.6
			1	22.1	140	113	8.18	222.5
			2	22	140.4	111.8	8.16	221
			3	19	133.7	121.5	8.07	225
			4	16	126.4	127	7.89	227
			5	12.5	124.5	118	7.78	228.9
			6	9.8	122.7	120	7.78	229.7
			7	9	124.1	86	8.67	227

Table D-1: Continued

Lake Name	Easting	Northing	Depth (m)	Temperature	Conductivity	DO%	pH	ORP
Nichol Lake	605881	5244401	0	22	123.4	132.3	8.09	207.5
			1	21.4	121.4	132.7	7.96	208
			2	21.7	125.2	130.1	10.63	210
Pine Lake West	604042	5235854	0	21.7	90	150	8.25	204
			1	21.7	90	-	8.23	204
			2	21.6	89.7	-	8.24	204.1
			3	21.2	88.3	-	8.25	204.9
			4	19.7	84.5	-	8.19	207.9
			5	13	73.9	-	8.07	216.8
			6	8.2	66.2	-	7.94	221.7
			7	7	64.2	-	7.9	222.8
			8	5.9	62.3	-	7.87	222.6
			9	5.7	61.9	-	7.85	221
Pine Lake East	605697	5235453	0	21.4	89.5	133.8	8.02	206.2
			1	21.4	89.6	129.8	8.01	205.6
			2	21.4	89.5	125.2	8.01	204
			3	21.4	89.3	123.6	7.97	204.6
			4	21.1	89	120.7	7.96	205.1
			5	17.3	80.2	145.6	7.79	208.4
			6	10.6	72.8	146.1	7.58	220.4
			7	6.5	64	161.4	7.46	222.2

Table D-2: Water Geochemical data from Cobalt and Silver Center.

Lake Name/Parameter	Alkalinity	Cl	SO4	Ca	Mg	Na	K	Al	Sb	As
Reference Method	SM2320B	SM4110C	SM4110C	SM3120	SM3120	SM3120	SM3120	SM3120	EPA200.8	EPA200.8
Units	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Brady Lake	100000	600	7000	35200	6870	900	600	20	3.7	140
Mary Ann Lake	86000	500	2000	26700	6630	900	300	40	0.1	0.9
Frog Lake	58000	600	2000	19100	4890	900	200	40	0.2	0.7
Clear Lake	68000	30900	5000	24800	3870	19900	400	10	0.2	2
Green Lake	59000	17600	3000	20100	4400	12600	400	30	0.2	2.9
S. Peterson Lake	103000	800	6000	31400	7670	1300	800	10	4.6	297
N. Peterson Lake	107000	800	6000	32200	8080	1400	800	10	5	312
Kerr Lake	127000	1100	34000	47800	12000	3500	1200	10	12.1	348
Fourclaim Lake	42000	500	4000	14500	2090	900	700	20	6.3	542
North Pickerel Lake	74000	600	6000	26300	3750	800	200	30	0.2	5
South Pickerel Lake	70000	600	5000	24400	3580	700	200	40	0.2	3.3
Oxbow Lake	6000	500	3000	3520	910	800	200	70	0.1	0.7
Maidens Lake	28000	10600	4000	11500	4250	2000	300	20	0.4	23.6
Cart Lake	76000	500	6000	21000	6910	1800	900	20	6.9	972
Tooth Lake	28000	500	4000	9240	1920	800	300	20	0.4	635
Ice Chisel Lake	5000	500	1000	360	120	200	300	20	0.1	1.7
Kirk Lake #1	66000	500	3000	21100	4880	700	300	30	1	34
Kirk Lake #2	67000	500	3000	20700	4790	700	300	30	1	32.6
Kirk Lake #3	66000	600	3000	21800	4910	800	300	130	2	79.8
Silver Lake	60000	500	2000	21900	5815	1500	300	90	0.1	7.3
Ibsen Pond	70000	500	3000	24900	6240	2300	200	70	0.7	142
New Lake Middle	41000	500	3000	13900	3810	700	200	30	0.4	36.8
New Lake North	40000	500	3000	13200	3710	800	200	30	0.4	36.6
Crosswise Lake	66000	500	3000	20700	5060	800	300	40	1	82.4
Cobalt Lake	129000	22100	10000	49000	9220	17400	1000	70	12.9	495
Goodwin Lake	72000	500	3000	23000	5470	700	200	20	0.1	1.4
Nichol Lake	64500	600	1000	22700	5620	1350	350	90	0.1	0.7
Pine Lake West	43000	500	3000	18700	4210	2000	300	70	0.3	0.4
Pine Lake East	43500	550	3000	17150	4190	750	250	45	0.15	2.05

Table D-2: Continued

Lake Name/Parameter	Cd	Co	Cu	Fe	Pb	Mo	Ni	Ag	U	Zn
Reference Method	EPA200.8	EPA200.8	EPA200.8	SM3120	EPA200.8	EPA200.8	EPA200.8	EPA200.8	EPA200.8	SM3120
Units	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Brady Lake	0.02	1.1	0.1	51	0.06	0.5	2.1	0.02	0.05	5
Mary Ann Lake	0.02	0.1	0.1	67	0.09	0.1	0.7	0.02	0.06	5
Frog Lake	0.02	0.1	0.2	35	0.02	0.1	0.6	0.02	0.05	5
Clear Lake	0.02	0.1	0.1	12	0.02	0.1	0.5	0.02	0.05	5
Green Lake	0.02	0.1	0.1	61	0.11	0.1	0.7	0.02	0.05	5
S. Peterson Lake	0.02	1	1.1	22	0.02	1.2	5.2	0.02	0.15	12
N. Peterson Lake	0.02	0.9	2.1	22	0.02	1.2	7.6	0.02	0.17	5
Kerr Lake	0.04	624	0.9	5	0.02	2.2	120	0.02	0.53	53
Fourclaim Lake	0.02	0.8	0.1	38	0.02	1	3.6	0.02	0.05	8
North Pickerel Lake	0.02	0.1	0.5	14	0.16	0.3	0.9	0.02	0.05	5
South Pickerel Lake	0.02	0.1	0.9	15	0.29	0.2	0.8	0.02	0.05	5
Oxbow Lake	0.02	0.1	0.1	37	0.78	0.1	0.5	0.02	0.05	16
Maidens Lake	0.02	0.1	0.6	5	0.02	0.1	1.3	0.02	0.05	6
Cart Lake	0.02	1.7	1.6	45	0.35	2.4	5.3	0.05	0.14	5
Tooth Lake	0.02	0.1	0.1	5	0.02	0.3	0.8	0.02	0.05	12
Ice Chisel Lake	0.02	0.1	0.1	34	0.13	0.1	0.5	0.02	0.05	10
Kirk Lake #1	0.02	0.2	0.7	36	0.06	0.4	1.3	0.02	0.16	12
Kirk Lake #2	0.02	0.2	0.6	37	0.06	0.3	1.3	0.02	0.15	8
Kirk Lake #3	0.02	4	3	203	2.38	0.4	2.9	0.23	0.15	57
Silver Lake	0.24	0.35	1.05	140	0.425	0.2	2.1	0.04	0.4	35.5
Ibsen Pond	0.37	10.5	1.5	251	0.84	0.4	7.8	0.03	0.6	32
New Lake Middle	0.02	1.8	0.3	21	0.03	0.2	2.9	0.02	0.05	20
New Lake North	0.02	2.2	0.2	13	0.11	0.2	3.1	0.02	0.05	9
Crosswise Lake	0.02	0.3	1.2	31	0.18	0.3	2.5	0.02	0.1	9
Cobalt Lake	0.41	2.7	2.3	188	0.54	2.8	10.2	0.02	0.89	38
Goodwin Lake	0.02	0.1	0.1	9	0.02	0.2	1	0.02	0.14	9
Nichol Lake	0.11	0.2	1.6	109.5	1.27	0.15	5.65	0.025	0.885	23
Pine Lake West	0.02	0.1	0.1	174	0.02	0.1	0.7	0.02	0.07	53
Pine Lake East	0.02	0.35	1.15	42	0.76	0.15	1.25	0.02	0.095	24

Table D-2: Continued

Lake Name	Anion Sum	Cation Sum	% Difference	Ion Ratio	Na Adsorption Ratio	TDS (ion sum	Conductivity	pH	Depth	Temperature
Reference Method	calc.	calc.	calc.	calc.	calc.	calc.	calc.	field	field	field
Units	meq/L	meq/L	%	AS/CS		mg/L	µmho/cm		feet	°C
Brady Lake	2.18	2.39	4.57	0.913	0.0378	112	220	8.7	8	19.6
Mary Ann Lake	1.77	1.99	5.84	0.89	0.0442	89.8	181	7.2	4.2	20.5
Frog Lake	1.24	1.41	6.2	0.883	0.0502	63.6	129	6.9	42	19.3
Clear Lake	2.33	2.48	3.26	0.937	1	126	253	8.05	50	19.4
Green Lake	1.73	1.93	5.49	0.896	0.668	93.6	190	8.47	17.6	21.7
S. Peterson Lake	2.21	2.37	3.52	0.932	0.057	111	220	8.32	18	19.8
N. Peterson Lake	2.29	2.45	3.43	0.934	0.0682	115	227	7.97	22	19.4
Kerr Lake	3.29	3.56	3.88	0.925	0.117	177	334	8.95	32	19.2
Fourclaim Lake	0.933	0.956	1.23	0.976	0.0588	47.9	95	8.2	14	23.1
North Pickerel Lake	1.63	1.66	0.938	0.981	0.038	82.3	161	8.7	6.5	19.9
South Pickerel Lake	1.54	1.55	0.404	0.992	0.0372	77.4	152	8.52	8.9	19.9
Oxbow Lake	0.198	0.294	19.5	0.674	0.104	12.6	27	7.15	5.3	20.4
Maidens Lake	0.929	1.02	4.47	0.914	0.126	48.8	105	7.84	30.8	21.5
Cart Lake	1.67	1.72	1.43	0.972	0.088	83.4	165	8.89	4	18.6
Tooth Lake	0.666	0.663	0.183	1	0.0625	34	68.1	7.66	56.3	22
Ice Chisel Lake	0.038	0.0432	6.37	0.88	0.0403	2.6	5.29	4.7	50	19.9
Kirk Lake #1	1.4	1.5	3.57	0.931	0.0377	70	141	8.06	39	20.7
Kirk Lake #2	1.41	1.47	1.88	0.963	0.0348	69.9	140	8.06	39	20.7
Kirk Lake #3	1.4	1.54	4.74	0.91	0.0384	71.4	144	8.06	39	20.7
Silver Lake	1.25	1.655	13.45	0.7685	0.0707	67.8	142	8.75	4	21
Ibsen Pond	1.45	1.87	12.7	0.774	0.105	78.4	161	8.75	14.8	21.4
New Lake Middle	0.906	1.04	7.1	0.867	0.0454	47.2	97.5	8	63	21.9
New Lake North	0.88	1	6.63	0.876	0.0501	45.7	94.3	8.25	14	22.9
Crosswise Lake	1.39	1.49	3.78	0.927	0.0409	69.7	141	8.1	24.2	21.8
Cobalt Lake	3.4	4	7.99	0.852	0.598	186	366	8.34	34	22
Goodwin Lake	1.51	1.63	3.88	0.925	0.0338	75.8	153	8.28	25	22
Nichol Lake	1.335	1.67	10.59	0.816	0.06595	70.85	147	9.17	6.75	22
Pine Lake West	0.932	1.38	19.6	0.673	0.111	54.6	116	8.13	42	21.7
Pine Lake East	0.957	1.24	12.71	0.778	0.0442	52.8	110.5	8.24	15	21.4

Table D-3: Sediment Geochemical Data. All concentrations in mg/kg. Reference methods are all EPA, * indicates both EPA 6010 and 6020 used for tailings and lake sediment, respectively.

Lake	Depth	Sb	As	Ba	B	Bi	Bo	Cd	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Se	Ag	Tl	Ti	U	V	Zn
Ref. Method		6020	6020*	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6020	6020*	6020	6010	6020	6010	6010
Mary Anne	0-5	1.7	13	39	0.2	5	13.7	2.1	19	9	78	8520	55	64	2	49	3.1	1.2	0.2	133	2.1	9	162
Mary Anne	20	0.5	1.4	56	0.2	5	9.8	0.7	23	4	45	4530	5	47	1	28	1.1	0.2	0.1	145	1.8	7	75
Mary Anne	40	0.5	1.8	66	0.2	5	10.8	0.8	29	6	46	6300	5	69	1	28	1.3	0.2	0.1	194	1.5	10	104
Frog	0-3	0.5	10.4	64	0.3	5	8.4	1.4	42	9	65	10800	30	273	1	34	1.9	1.7	0.1	264	2.1	14	145
Frog	5	0.5	6.8	60	0.3	5	7.6	0.9	43	7	59	9260	15	222	1	27	2	1.7	0.1	280	3.1	15	125
Frog	20	0.5	5.6	72	0.4	5	9.7	1.1	52	9	76	10900	14	210	1	31	1.9	1.5	0.1	279	3.2	22	150
Frog	50	0.5	7.8	70	0.4	5	10.3	1.1	53	11	87	11200	14	203	1	32	2.5	1.5	0.2	309	3.6	25	156
Green	0-5	3.8	109	39	0.2	5	10.3	2.8	19	27	113	16300	99	235	2	63	4.4	3.3	0.2	137	0.9	15	224
Green	34	0.5	1.8	34	0.2	5	9.7	0.8	16	6	64	4310	6	58	2	22	1.7	0.2	0.1	98	1.1	11	124
Green	72	0.5	1.8	33	0.2	5	10.8	1	18	6	72	5990	7	70	2	25	1.9	0.2	0.1	112	1.2	11	144
Goodwin	0-3	0.8	9.5	64	0.5	5	9.4	2	45	11	70	15700	66	346	1	41	2.3	0.7	0.2	291	4	20	154
Goodwin	5	0.5	2.6	55	0.4	5	7.8	0.8	39	7	45	10200	12	218	1	22	1.4	0.2	0.1	230	4.3	18	103
Goodwin	20	0.5	1.2	57	0.5	5	9.8	0.8	47	7	56	10400	6	175	1	24	1.5	0.2	0.1	280	4.8	21	105
Goodwin	25	0.5	2	59	0.5	5	9.6	0.8	46	7	55	10800	9	188	1	25	1.6	0.2	0.1	282	4.9	21	125
East Pine	0-3	0.5	3.9	41	0.2	5	6.4	0.6	18	3	65	8820	13	275	1	23	2.7	0.2	0.1	173	4.6	10	50
East Pine	5	0.5	1.2	43	0.2	5	4.1	0.5	9	1	44	4440	5	269	1	11	1.8	0.2	0.1	78	5.2	6	23
East Pine	20	0.5	0.5	67	0.2	5	1.7	0.5	3	1	35	1240	5	228	1	6	0.7	0.2	0.1	24	2.6	2	10
East Pine	28-1	0.5	0.5	60	0.2	5	3.1	0.5	4	1	38	1840	5	273	1	8	1.1	0.2	0.1	31	5.9	3	18
East Pine	28(2)	0.5	0.5	60	0.2	5	2.8	0.5	4	1	36	1660	5	263	1	8	1	0.2	0.1	27	5.4	3	17
Oxbow	0-5	0.8	12.4	53	0.4	5	6.8	2.7	22	12	69	9180	72	263	2	56	3.1	0.4	0.2	108	1.2	10	161
Oxbow	20	0.5	6.6	52	0.5	5	5.7	0.9	27	12	58	4430	13	130	2	33	2.4	0.2	0.1	113	2.1	12	97
Oxbow	32	0.5	6.9	49	0.5	5	5.4	0.9	28	16	63	4980	13	128	2	34	2.3	0.2	0.1	122	2.1	12	194
S. Pickerel	0-3	2	48	18	0.2	5	9.9	3.8	18	11	126	9640	120	100	2	60	5.3	3	0.2	141	1	12	268
S. Pickerel	20	0.5	10	18	0.2	5	6	0.8	14	3	89	5680	5	50	2	14	1.8	0.2	0.1	86	1.3	14	106
S. Pickerel	63	0.5	12	31	0.2	5	5	0.7	21	3	149	6110	5	71	3	24	2.1	0.2	0.1	160	1.7	15	80
Nichol	0-1	1	12.8	37	0.2	5	8.9	3.1	17	6	80	5020	98	37	2	46	3.6	0.9	0.2	99	2.2	11	144
Nichol	4	1.1	15	42	0.3	5	6.1	1.9	20	7	69	4050	49	35	2	31	2.9	0.8	0.2	109	3.5	13	119
Nichol	20	0.5	1	45	0.2	5	12.8	0.5	16	2	70	5230	5	29	4	16	2.4	0.2	0.1	88	5.2	12	64
Nichol	54	0.5	0.8	48	0.2	5	21	0.8	10	2	102	2900	5	29	4	13	2.8	0.2	0.1	51	9.7	10	112
Ice Chisel	0-1	0.5	3.2	58	0.4	5	2.9	0.7	44	8	36	13500	9	149	1	30	1.4	0.2	0.1	456	1.3	31	118
Ice Chisel	5	0.5	2.2	71	0.5	5	3	0.5	49	9	36	15200	7	178	1	31	1.3	0.2	0.1	581	2.1	32	83
Ice Chisel	10.5	0.5	4.1	55	0.5	5	3.1	0.5	38	7	34	11300	6	149	1	24	1.8	0.2	0.1	500	2	33	64
West Pine	0-3	1	12	69	0.7	5	8.6	1.3	50	12	57	26100	38	405	1	33	2.9	0.7	0.3	218	6.1	30	129
West Pine	5	0.5	6.4	71	0.8	5	7.4	0.7	54	9	60	17600	14	363	1	30	2.4	0.5	0.3	203	6.6	32	109
West Pine	20	0.5	3.7	70	0.7	5	8.3	0.7	60	9	63	16100	10	358	1	33	2.4	0.5	0.2	248	6.9	34	105
West Pine	34	0.5	4.2	71	0.7	5	8.2	0.7	59	10	62	16000	13	358	1	33	2.5	0.6	0.2	248	6.7	33	116

Table D-3: Continued.

Lake	Depth	Sb	As	Ba	B	Bi	Bo	Cd	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Se	Ag	Tl	Ti	U	V	Zn
Ref. Method		6020	6020*	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6020	6020*	6020	6010	6020	6010	6010
N. New	0-3	11.8	236	25	0.2	5	16.7	4.4	27	64	183	9860	104	135	4	91	4	10.8	0.3	159	1.4	18	285
N. New	5	21.7	260	38	0.3	14	13.6	3.5	45	91	237	21100	159	260	4	89	2.7	25.1	0.2	392	2.1	46	237
N. New	20	2.4	33	54	0.2	5	15.3	1.3	22	16	74	4450	19	90	2	34	2.1	2.8	0.1	109	1.6	9	149
Middle New	0-5	13.1	492	51	0.3	7	10.7	7.4	39	107	130	14500	140	413	3	56	2	10.4	0.1	259	1.6	35	195
Middle New	20	2.4	131	69	0.3	5	12.5	2.5	34	80	93	8790	35	305	3	33	1.7	3.3	0.1	170	1.4	29	173
Middle New	57	0.5	11.1	54	0.3	5	13.9	1.1	41	12	71	9180	17	312	2	28	1.6	1.8	0.1	169	1.5	26	200
N. Pickerel	0-3	0.9	27	31	0.2	5	5.1	1.5	19	5	116	7560	25	81	3	29	2.3	0.8	0.1	120	1.1	13	154
N. Pickerel	5	0.7	19	31	0.2	5	5	1	19	3	114	6310	10	74	3	25	2.5	0.4	0.1	111	1.5	14	115
N. Pickerel	20	0.5	11.2	26	0.2	5	4.3	0.6	14	2	100	4090	5	49	3	19	1.7	0.2	0.1	79	1.3	12	92
N. Pickerel	62	0.5	12	32	0.2	5	4.3	0.6	22	4	145	6170	5	72	3	24	2.3	0.2	0.1	166	2	16	82
Silver	0-4	0.7	23	44	0.2	5	8.9	1.6	14	10	46	3380	33	50	2	40	2.2	1.1	0.1	82	2.2	7	101
Silver	20	0.5	1.4	49	0.2	5	8.7	0.7	19	4	45	3010	5	44	2	21	1.5	0.2	0.1	86	2.6	8	83
Silver	55	0.5	9	76	0.2	5	9.7	1.3	22	12	66	7440	28	266	2	23	1.6	1.2	0.1	136	2.2	12	193
N. Peterson	0-5	105	2650	52	1.2	27	8.1	14.9	124	569	5030	68900	377	863	6	1860	2.6	189	0.2	721	2.3	119	496
N. Peterson	20	8.8	335	25	0.3	5	15.4	1.9	35	70	374	10200	28	244	3	149	1.8	11.6	0.1	144	1.9	19	100
N. Peterson	38	6.2	134	27	0.4	5	15.4	1.2	31	36	107	7150	7	195	3	49	2	1.7	0.1	147	2	15	75
Clear	0-1	0.5	11	29	0.3	5	7.2	0.5	37	13	71	21800	6	420	1	40	2.3	0.2	0.2	418	2.1	23	77
Clear	0-1	0.5	11	31	0.3	5	7.3	0.5	36	12	73	23300	6	443	1	39	2.1	0.2	0.1	405	2	23	76
Clear	5	0.5	12.3	33	0.3	5	11.6	0.5	32	8	82	16900	5	441	2	37	2.7	0.2	0.2	346	2.7	22	64
Clear	20	2.2	37	106	0.7	5	7.2	0.5	87	26	68	38000	16	467	1	61	0.7	5.1	0.2	1250	2	48	100
Clear	38	0.5	0.5	18	0.2	5	11.1	0.5	27	6	91	17000	5	219	4	33	1.4	0.2	0.1	336	0.1	20	64
Brady	0-3	85.3	1950	47	0.5	24	9.1	8.7	84	387	209	65900	224	782	5	108	1.1	71.8	0.2	895	0.8	120	330
Brady	5	15.4	470	38	0.2	5	14.1	3.5	25	57	79	11300	66	229	3	31	2	10.6	0.2	133	1.1	24	181
Brady	20	0.8	13	42	0.2	5	14.4	0.8	22	8	46	4540	7	142	1	19	1.5	0.7	0.1	113	1	13	110
Brady	40	0.5	4.8	39	0.2	5	11.3	0.8	20	10	47	3980	5	67	1	17	1.8	0.3	0.1	81	1.3	11	148
Crosswise	0-2	35.9	1020	67	1.4	30	6.3	5.7	149	409	1400	79600	343	901	5	996	1.5	99	0.2	1370	2.6	134	320
Crosswise	0-2(2)	28.4	1020	65	1.4	30	6.3	5.6	148	408	1390	81400	336	892	5	995	1.1	76.8	0.1	1380	1.9	133	313
Crosswise	5	37.9	584	81	0.7	8	8.2	2.4	99	128	465	50800	90	722	2	164	1.1	94.2	0.2	1400	1.9	83	139
Crosswise	5(2)	28	634	82	0.7	9	8.1	2.8	103	133	505	56000	98	729	2	171	0.7	72	0.1	1430	1.3	88	145
Crosswise	20	0.5	4.4	31	0.3	5	12.7	0.5	32	7	109	17800	5	283	4	41	2.2	0.2	0.2	423	3.6	24	65
Crosswise	36	0.5	8.7	103	0.7	5	8.3	0.5	89	20	49	41300	11	455	1	55	0.7	0.7	0.2	1440	1.5	51	113
Maidens Lake	0-4	6	185	51	0.5	5	6.4	3.1	40	56	120	13600	78	203	3	69	3.6	2.6	0.2	220	3.3	26	163
Maidens Lake	7	1.7	59	43	0.5	5	6.3	1.3	34	22	105	8920	25	174	2	36	2.4	0.9	0.1	165	2.9	26	99
Maidens Lake	20	0.5	9.3	64	0.6	5	7.1	0.6	49	12	97	14200	6	169	4	33	2.4	0.4	0.1	394	4.5	31	78
Maidens Lake	33	0.5	1.7	24	0.3	5	2.5	0.5	28	8	32	14100	5	147	2	18	0.5	0.2	0.1	337	1.4	25	47
Maidens Lake	41	0.5	4.4	75	0.7	5	6.1	0.9	53	13	113	17300	5	177	8	33	2	0.3	0.1	338	4.4	33	103
Kerr	0-1	12.9	702	21	0.3	5	9	6	38	583	107	16200	78	600	1	145	1	10.8	0.1	188	1.2	21	637
Kerr	3	6.3	185	9	0.2	5	4.5	1.2	25	121	27	10300	22	247	1	38	0.5	2.5	0.1	217	0.7	15	227
Kerr	6	2.6	80	6	0.2	5	2.8	0.7	19	54	14	8370	12	180	1	22	0.5	1.1	0.1	295	0.4	13	116

Table D-3: Continued.

Lake	Depth	Sb	As	Ba	B	Bi	Bo	Cd	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Se	Ag	Tl	Ti	U	V	Zn
Ref. Method		6020	6020*	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6020	6020*	6020	6010	6020	6010	6010
Tooth #1	0-1	0.5	140	17	0.2	5	1.7	1.8	21	9	11	9120	13	271	1	17	0.6	0.3	0.1	256	0.6	13	50
Tooth #1	3	0.5	37	111	0.5	5	3	0.5	54	17	17	25000	8	334	1	37	0.5	0.2	0.1	771	1	33	74
Tooth #1	4	0.5	13.3	227	0.7	5	5.6	0.5	98	25	57	39400	11	563	1	61	0.9	0.2	0.3	1530	1.9	65	91
Tooth #1	20	0.5	3.8	176	0.7	5	6.4	0.5	97	23	42	36800	11	645	1	59	0.5	0.2	0.2	1610	1	61	77
Tooth #1	50	0.5	2.6	178	0.6	5	8.1	0.5	101	22	44	38000	10	804	1	62	0.5	0.2	0.2	1520	0.9	60	77
Tooth #2	0-1	0.5	34	14	0.2	5	0.9	0.5	14	6	7	6820	8	133	1	11	0.5	0.2	0.1	343	0.5	12	29
Tooth #2	0-1(2)	0.5	27	54	0.3	5	1.9	0.5	29	10	14	12700	7	209	1	21	0.5	0.2	0.1	495	1.7	19	46
Tooth #2	4	0.5	13	223	0.8	5	7.3	0.5	98	27	40	54400	12	712	1	62	0.5	0.3	0.2	1710	1	65	83
Tooth #2	18	0.5	8.1	193	0.7	5	7.2	0.5	97	25	44	52000	12	725	1	61	0.5	0.2	0.2	1620	1.9	64	77
Cart	0-3	31.1	4510	24	1.4	18	6.3	48.2	172	623	253	67400	332	827	8	259	0.9	51	0.1	808	1.6	168	473
Cart	9	35.5	965	23	1.4	16	4.9	10.5	154	327	171	65400	230	836	4	234	0.7	39.6	0.1	1280	1.6	160	249
Cart	13	48.3	1310	22	1	9	7.1	14.5	116	341	292	42300	161	627	8	224	1.3	32.6	0.1	713	2.1	103	388
Cart	19	20.1	915	27	0.5	5	14.2	10.6	53	204	471	20800	69	351	6	145	2.6	47.7	0.1	249	3.2	44	741
Cart	30	6.1	169	23	0.2	5	16.8	2.8	20	54	315	6700	9	180	4	43	2.8	3.5	0.1	99	3	11	188
Cart	45	52.8	1650	21	1.3	12	5	17.5	146	393	249	54700	207	809	9	257	1	38	0.1	987	1.9	134	382
Cart	69	24.4	522	34	0.6	8	14.8	6.4	63	145	238	21400	98	313	5	90	2.4	13.9	0.1	408	3.5	47	226
Ibsen	0-1	14.8	3490	37	0.5	39	9	38.1	75	961	386	39700	292	592	5	160	2.2	59.1	0.2	479	2	87	293
Ibsen	9	18.6	1840	35	0.6	46	9.3	20.8	87	515	427	45300	337	671	6	117	1.8	69.1	0.2	768	2.2	105	295
Ibsen	12	27	936	33	0.8	66	8.4	10.9	120	337	655	57300	420	933	6	133	1.3	102	0.2	1440	2.6	158	334
Ibsen	14	33.3	950	31	0.9	70	7.8	10.8	133	308	716	63500	435	996	6	146	1.2	109	0.2	1830	3.2	183	325
Ibsen	15	43.4	1340	38	1.1	83	7.8	14.4	153	383	789	70700	561	1200	7	192	0.9	122	0.2	2460	3.7	221	361
Ibsen	16	46.6	1440	41	1.2	82	7.8	15.5	155	389	842	73300	646	1210	7	204	0.9	127	0.2	2560	4.4	229	367
Ibsen	17	44.8	1450	42	1.2	80	8.6	15.4	154	383	845	72700	640	1200	7	198	1	129	0.2	2410	4.4	225	371
Ibsen	19	16.4	653	40	0.5	28	11.1	7.9	66	191	323	26700	235	527	4	92	1.2	43.5	0.1	498	2.6	78	213
Ibsen	30	2.4	315	58	0.4	17	9.6	4.4	50	101	202	17700	145	382	3	59	1.8	26.8	0.1	337	1.4	51	190
Ibsen	38	10.3	122	72	0.3	7	9.1	2.5	36	50	117	11500	72	305	2	39	1.2	11.1	0.1	212	2.4	28	173
Fourclaim	0-3	55.7	7420	46	1.1	151	7.3	36.3	398	1510	283	77300	107	1350	7	669	1.5	146	0.1	674	1.3	119	247
Fourclaim	5	56.4	5380	45	1	116	7.3	31.5	313	1180	245	58300	87	1030	6	524	2	135	0.2	475	1.6	94	213
Fourclaim	25	1.1	64	59	0.4	5	6.9	1.3	31	10	133	4400	28	81	2	32	2.2	1.1	0.1	84	1.5	10	148
Fourclaim	48	1	83	66	0.5	5	6.4	1.6	34	12	133	5750	33	84	3	35	2.4	1.2	0.1	86	1.8	11	264
South Peterson	0-2	52	2430	35	1.4	54	7.8	15	114	726	1100	68300	879	792	5	436	1.6	199	0.1	397	1.8	124	863
South Peterson	0-2(2)	51.4	2450	35	1.4	55	7.6	15.8	114	733	1100	68500	882	792	5	439	1.6	196	0.1	395	1.9	123	863
South Peterson	4	88.5	3290	32	1.6	61	7.7	19.5	128	708	1120	78900	1030	745	6	408	1.3	255	0.1	497	2.3	146	1040
South Peterson	14	52.3	1560	30	2.2	96	5.7	9.6	150	465	1050	86900	1850	719	5	226	0.6	237	0.1	683	2.2	163	998
South Peterson	24	79	2050	28	1.6	54	11.1	14.6	109	431	861	59200	1080	552	4	240	1.2	203	0.1	427	2.3	119	871
South Peterson	41	4	170	27	0.4	5	13.6	1.2	38	36	94	8590	14	187	3	39	1.9	1.6	0.1	130	2.1	15	79
South Peterson	41(2)	4	174	27	0.4	5	13.9	1.2	39	36	97	8840	15	191	3	40	2	1.7	0.1	134	2.2	15	77
South Peterson	59	3.8	177	25	0.3	5	14.5	1.4	46	42	90	10300	11	190	3	43	2.3	1.2	0.1	163	2.4	17	81
South Peterson	63	8.3	234	27	0.4	5	15.6	1.7	46	53	127	11500	66	204	3	48	2.5	9.7	0.1	195	2.6	23	124

Table D-3: Continued.

Lake	Depth	Sb	As	Ba	B	Bi	Bo	Cd	Cr	Co	Cu	Fe	Pb	Mn	Mo	Ni	Se	Ag	Tl	Ti	U	V	Zn
Ref. Method		6020	6020*	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6010	6020	6020*	6020	6010	6020	6010	6010
Cobalt	0-3	97.5	10800	17	1	58	6.1	54	133	2070	575	74100	274	827	25	719	1	103	0.1	590	2.2	107	551
Cobalt	4	71.9	8050	14	0.9	50	5.2	37.6	128	1710	519	68700	240	777	22	635	0.7	84.7	0.1	612	1.7	103	417
Cobalt	10	34.5	1090	8	0.8	21	3.1	6	117	498	220	59100	114	630	9	252	0.5	43.1	0.1	732	1.3	98	167
Kirk Lake-1	0-3	41.2	1160	48	0.8	42	6.7	13.6	119	458	357	55600	302	998	6	197	1.4	90.3	0.2	1280	2.1	138	257
Kirk Lake-1	20	2.1	44	68	0.5	5	7.9	0.9	68	34	71	24000	17	358	2	50	1.8	3.4	0.2	915	5.3	38	97
Kirk Lake-1	39	2.5	43	74	0.5	5	8.5	0.8	68	32	73	23500	19	367	2	49	2.1	3.8	0.2	911	7.1	39	108
Kirk Lake-2	0-2	58.3	3630	31	0.9	49	6.4	38.9	130	823	251	62800	242	1090	14	378	1	102	0.1	863	1.5	148	248
Kirk Lake-2	20	64.7	1240	37	1	64	6.1	13.9	151	365	651	69300	360	1370	7	224	1	130	0.2	2040	2.2	186	265
Kirk Lake-2	29	56.3	1160	41	1	52	6.6	12.8	145	325	563	65800	300	1370	7	209	0.9	121	0.2	1990	2.2	180	232
Kirk Lake-2	31	16.5	260	66	0.6	10	8.8	3.6	67	64	144	24400	89	567	2	61	1.3	22	0.2	699	4	59	113
Kirk Lake-3	0-2	63.1	2180	48	0.8	55	7.7	11.4	117	500	375	76800	411	1010	4	175	1.1	120	0.2	1350	1.5	160	315
Kirk Lake-3	18	17.9	381	53	0.6	14	8.1	1.9	69	106	177	33000	94	545	3	78	1.1	31.4	0.1	659	4.7	64	125

Appendix E: Supplementary Figures

Figure E-1: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Clear Lake.

Figure E-2: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Green Lake.

Figure E-3: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for North Pickerel Lake.

Figure E-4: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for South Pickerel Lake.

Figure E-5: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Nichol Lake.

Figure E-6: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Silver Lake.

Figure E-7: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Goodwin Lake.

Figure E-8: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Mary Anne Lake.

Figure E-9: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Frog Lake.

Figure E-10: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for Ice Chisel Lake.

Figure E-11: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver profile for East Pine Lake.

Figure E-12: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver for West Pine Lake.

Figure E-13: Geochemical core profile of arsenic, antimony, cobalt, nickel and silver for Oxbow Lake.

Figure E-14 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Clear Lake and b) Green Lake.

Figure E-15 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) North Pickerel Lake and b) South Pickerel Lake.

Figure E-16 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Nichol Lake and b) Silver Lake.

Figure E-17 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Goodwin Lake and b) Mary Anne Lake.

Figure E-18 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Frog Lake and b) Ice Chisel Lake.

Figure E-19 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) East Pine Lake and b) West Pine Lake.

Figure E-20 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Cart Lake and b) Brady Lake.

Figure E-21 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) South Peterson Lake and b) North Peterson Lake.

Figure E-22 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Ibsen Pond and b) Fourclaim Lake.

Figure E-23 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Cobalt Lake and b) Kerr Lake.

Figure E-24 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Maidens Lake and b) Crosswise Lake.

Figure E-25 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Tooth Lake 1 and b) Tooth Lake 2.

Figure E-26 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) New Lake Middle and b) New Lake North.

Figure E-27 a-b: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for a) Kirk Lake 1 and b) Kirk Lake 2.

Figure E-28: Arsenic concentration, organic content (%dry weight) and water content (%wet weight) for Kirk Lake 3.