The role of iron and anthropogenic activities in eutrophication: a contemporary and paleolimnological study

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ABSTRACT

In this study, I examined water chemistry of 31 Canadian Shield lakes in relation to catchment characteristics to test the hypothesis that Shield lakes with more marble may exhibit iron (Fe) deficiency and, hence, be more vulnerable to eutrophication. I performed a diatom-based paleolimnological reconstruction of one of these lakes (Heney Lake), which was subjected to anthropogenic stresses including a fish farm. Results suggest that the presence of marble influenced lake chemistry, including lowering the ratio of Fe: P. The reconstruction of historical P concentrations was not statistically possible but past Fe could be inferred, which no previous study has attempted. Certain eutrophication-associated diatom species suggest that logging and European settlement beginning in the early XXth century led to a slight increase in nutrient concentrations. However, a more important diatom species shift was likely related to climate change, as observed in other temperate lakes worldwide.

RÉSUMÉ

Dans cette étude, j'ai examiné la chimie de l'eau de 31 lacs du Bouclier Canadien en relation avec les propriétés de leur bassin versant pour tester l'hypothèse que les lacs avec davantage de marbre peuvent être plus déficients en fer (Fe), et donc plus vulnérables à l'eutrophisation. J'ai utilisé les diatomées pour élaborer une reconstruction paléolimnologique d'un de ces lacs (Heney), lequel a subi plusieurs pressions anthropiques incluant une pisciculture. Les résultats suggèrent que le marbre influence la chimie de l'eau, notamment en diminuant le ratio Fe: P. La reconstruction du P fut impossible pour des raisons statistiques, mais les concentrations en fer ont pu être reconstruites, ce qu'aucune étude n'avait accompli auparavant. Certaines diatomées associées à l'eutrophisation suggèrent que la coupe forestière et le développement du territoire ont augmenté les concentrations de nutriments. Finalement, l'étude suggère que les changements climatiques récents ont eu un effet important sur les diatomées.

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APLH	Association for the Protection of Lake Heney
CA: LA	Catchment area: lake area ratio
CAREG	Center for Advanced Research in Environmental Genomics
CFCS	Constant Flux Constant Sedimentation Rate
CIC	Constant Initial Rate
CRS	Constant Rate of Supply
DI	Diatom-inferred
DO	Dissolved oxygen
ELA	Experimental Lake Area
ESRI	Environmental Systems Research Institute
ICP-MS	Inductively Coupled Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LCM	Lakeshore Capacity Model
MDDECLL	Ministère du Développement Durable, de l'Environnement et Lutte contre les Changements Climatiques
ORP	Oxidation-reduction potential
PCA	Principal component analysis
TKN	Total Kjeldhal Nitrogen
TN	Total nitrogen
TP	Total phosphorus
RP	Reactive phosphorus
SIGEOM	*Système d'Information Géominière* du *Québec*

1. General introduction

1.1. Lake ecology

1.1.1. Nutrients and lake productivity

Surface waters, including rivers, lakes and reservoirs, are among the planet's most extensively altered ecosystems (Carpenter et al., 2011). Pressures include the loss of native species with the expansion of invasive species, changes to hydrological flow, morphological modifications and changes in the biogeochemical cycling of elements including nutrients that lead to eutrophication.

Eutrophication is a natural phenomenon of nutrient enrichment that occurs over centuries or millennia. Erosion and transport from the watershed and tributaries, atmospheric deposition and within-lake production are sources of nutrients, plant material and sediments that can slowly fill a lake basin (Callisto et al., 2014). Multiple characteristics of the water basin and its watershed, as well as the climate and the local geology, impact the timing of the eutrophication process, during which a lake gradually becomes a pond, then a marsh, then a meadow and finally dry land (Callisto et al., 2014). Cultural eutrophication on the other hand is the acceleration of lake productivity in response to the excessive addition of inorganic nutrients and organic matter due to human activities and represents a major environmental concern (Smith and Schindler, 2009). The key difference between natural and human-induced, or cultural eutrophication, is the timing. If natural eutrophication occurs over geological time scales, cultural eutrophication takes place over decades.

The main nutrient that causes eutrophication in freshwater systems is phosphorus (Schindler, 1974). Phosphorus (P) plays a critical role in biological metabolism yet occurs in relatively low amounts in the hydrosphere (Wetzel, 2001). In oligotrophic temperate lakes, P is the principal limiting nutrient for phytoplankton growth as it has the lowest supply to demand ratio (Kalff, 2002). Phosphorus therefore most commonly determines the trophic state of temperate freshwater ecosystems and is the main driver of eutrophication (Schindler, 1974). Nitrogen is also an essential element for life and is an important nutrient in freshwater ecosystems (Kalff, 2002). However, this element is more abundant and has multiple sources, including the atmosphere, that are potentially bioavailable (Vass et al., 2015). Only in eutrophic systems is the N: P supply ratio typically low enough to result in nitrogen limitation (Kalff, 2002).

Phosphorus occurs in different forms and fractions. Total phosphorus includes both particulate and dissolved forms. Particulate P is present in organisms, mineral phases such as ferric hydroxides, as well as adsorbed onto organic matter. Dissolved P includes inorganic orthophosphate (PO_4^{3-}) and organic colloids. Inputs of P to a lake from its watershed are mostly in the dissolved form, with some organic P incorporated to particles washed from land or added to wet and dry atmospheric deposition (Kalff, 2002). Orthophosphate is the principal bioavailable form of P.

Sources of P and other nutrients can be divided into point sources and nonpoint sources. Bedrock is probably the most important natural nonpoint source of P (Kalff, 2002). During the weathering process, the water-soluble phosphate ions are slowly released and transported to freshwater systems. Different rocks have varying P concentrations and so the geological composition of a water body's watershed can influence its natural P concentrations. For example, fresh waters in mountainous regions composed of crystalline bedrock typically have very low P concentrations while lowlands of sedimentary bedrock usually yield higher P (Wetzel, 2001). Vegetation cover in the watershed also has impacts on the P export to lakes and rivers. A well-vegetated catchment tends to retain nutrients so less nutrients are exported (Kalff, 2002). As a result the total phosphorus (TP) concentrations in uncontaminated surface water are variable, but typically range between 10 and 50 μg/L (Wetzel, 2001).

Numerous human activities have contributed to cultural eutrophication by increasing the nutrient inputs to freshwater through point and nonpoint sources (e.g. Callisto et al., 2014). Point sources of nutrient and chemical inputs to water bodies include wastewater effluent from municipal and industrial sources, runoff leachate from waste disposal sites, runoff and infiltration from animal feedlots, overflows of combined storm and sanitary sewers (Carpenter et al., 1998) as well as fish farming activities (Vass et al., 2015; Massik & Costello, 1995). Nonpoint or diffuse sources are more difficult to measure and regulate as they result from activities dispersed on large territories, and the pollutants may be transported overland, underground or through the atmosphere before they reach an aquatic ecosystem (Callisto et al., 2014). Agriculture represents the most important nonpoint source of nutrient inputs to aquatic systems (Carpenter et al., 1998). Phosphorus has been used extensively since the 1950s as a fertilizer and has contributed to major increases in global food production (Tilman et al., 2002). The concurrent livestock production and increase in fertilizer usage has more than tripled the global P flows to the biosphere compared to pre-industrial levels (Smil, 2000). In addition to agriculture, the increasing affluence that followed the Second World War allowed an increasing number of households to acquire dishwashers and washing machines, which used P-rich detergents (Kalff, 2002). Urban runoff also represents a significant nonpoint source as it transports nutrients from lawn fertilizers, pet waste and construction sites where erosion rates can be extremely high (Carpenter et al., 1998). According to the U.S. EPA (2000), urban runoff is the third most important nonpoint source of chemicals and nutrients to aquatic systems. To a usually smaller yet significant extent, nutrients also reach water bodies through atmospheric deposition. Although this represents a natural pathway, it captures nutrients from both natural and anthropogenic sources and has significantly increased with the intensification of human activities (Zhai et al, 2009). Natural atmospheric depositions include volcanic particles, pollen and forest fires, while anthropogenic sources mainly consists of coal burning, intensive fertilizer usage, phosphorus rock mining and the microbial reduction processes in sewage sludge, landfills, compost heaps (Winter et al., 2002).

Cultural eutrophication is considered the primary problem facing most surface waters today (Smith and Schindler, 2009). It is among the most visible human alteration to the biosphere (Smith, 2003) and can have multiple deleterious effects on aquatic ecosystems. Common impacts include reductions in water clarity, biodiversity declines (Maberly et al., 2002, Callisto et al., 2014), changes in macrophyte species composition and biomass, and increases in cyanobacterial blooms (O'Neil et al., 2012; Carpenter et al., 1998; Kalff, 2002). The increase in primary production further increases the amount of organic matter entering the hypolimnion (Nürnberg, 1995). The microbial decomposition of this organic matter consumes oxygen and may lead to bottom water anoxia (oxygen < 1 mg/L) and the concomitant release of toxic gases such as ammonia and hydrogen sulphide which have deleterious effects on fish and benthic invertebrates (Callisto et al., 2014). Other consequences of anoxia are changes in the geochemical conditions at the sediment-water interface that can instantly remobilize the previously sedimented P back into the water column, creating a positive feedback loop (Nürnberg, 1995). From a human perspective, eutrophication leads to serious water degradation problems, decreases in the availability of water for drinking, irrigation and industrial activities, as well as loss of recreational and aesthetic values of water bodies (Carpenter et al., 1998).

1.1.2. Iron and phosphorus cycling in lakes

In addition to phosphorus, iron is also an essential micronutrient for plants and phytoplankton: Fe is an important catalytic component for many enzymatic and electron transport systems (Kalff, 2002). Most of the iron taken up by algae is in its ferrous form (Fe^{2+}), which can be transported directly into the cell through a divalent metal transporter (Kustka et al., 2007). Some cyanobacteria have the advantage of using Fe^{3+} by means of the siderophores they produce (Murphy et al., 1976; Brown & Trick, 1992). These low molecular weight chelators have strong affinity for ferric iron (Hopkinson & Morel, 2009) and allow the cell to scavenge iron that is not available to its eukaryotic competitors (Molot et al, 2014). Nonetheless, some eukaryotic organisms including diatoms and green algae species have evolved mechanisms to take up Fe^{3+} through the use of enzymes, but the specific mechanisms are not well understood (Kustka et al., 2007).

In natural freshwater ecosystems, weathering of the bedrock and soil in the watershed provide most of the iron (e.g. Xing & Liu, 2011) as well as the calcium (Smol, 2010). The amount of iron exported depends on bedrock and soil composition, temperature, precipitation and hydrology (Davison, 1993). Atmospheric deposition may also contribute to a small fraction of the iron inputs to lakes (Salomons & Forstner, 1984). Once iron enters a lake, only a small portion will eventually discharge at the outflow as the vast majority remains within the lake. In fact, 70 to 90% of the iron entering a lake is ultimately accumulated in the sediments (Davison & Tipping, 1984). While iron is usually abundant, there are certain aquatic systems where it can limit phytoplankton growth (Kalff, 2002). About 40 % of the world's ocean experience iron limitation for phytoplankton growth (de Barr et al., 2005), particularly in high-nitrate low-chlorophyll areas such as the equatorial Pacific Ocean (Martin et al., 1994) and the north-east Pacific subarctic (Martin & Fitzwater, 1988). This phenomenon is less common in freshwater where photosynthetic communities are mainly controlled by macronutrients (Elser et al., 2007; Sterner, 2008). However, certain researchers have suggested that iron plays an important role in the control of cyanobacterial blooms (Molot et al., 2014), which are symptomatic of eutrophication.

Two oxidative states are possible for iron in aquatic environments (Davison, 1993). In its oxidized form, Fe^{3+} or ferric iron is insoluble and forms a number of insoluble oxides and hydroxides (FeOOH), which then sink and settle at the sediments surface (Kalff, 2002). As long as sufficient oxygen is present, surficial sediments remain oxidized and a characteristic rusty brown layer of ferric oxides may be observed (Burns & Ross, 1972). However, when respiration rates are high in superficial sediments, anoxia may occur before deoxygenation of the overlying water column. Once the dissolved oxygen, manganese and nitrate have been consumed as terminal electron acceptors for the microbial oxidation of organic matter, ferric iron may undergo chemical and microbial reduction. In its reduced form, ferrous iron (Fe^{2+}) is water-soluble and circulates back into the water column. The sediment depth interacting with with lake water varies depending on lake morphology, sediment characteristics and wind exposure (Søndergaard et al., 2003). In a majority of lakes, the upper approximately 10 cm is considered to take part in the whole lake mechanism (Boström et al., 1982), but mobile P has been observed in depths down to 20-25 cm (Søndergaard et al., 1999).

As first suggested by Einsele (1936; in Hupfer et al., 2007) and refined by Mortimer (1942), the P and Fe cycle are closely linked in freshwater systems. The classic Mortimer model describes that under oxic conditions, iron forms hydroxides that have a strong sorption capacity for P. The complex FeOOH~P is insoluble and sinks to the bottom, where it remains at the sediment-water interface for as long as oxic conditions are maintained (Mortimer, 1942). However, when oxygen concentrations drop and redox conditions get sufficiently low, iron in the hydroxide complex is reduced into its soluble form and returns to the water column, along with the P it was previously bound to, a phenomenon referred to as internal loading (Fig. 1). The release of the two elements is, in theory, roughly synchronous and in the same stoichiometric ratio (Gächter et al., 1988). Ferric complexes in the sediments would therefore be a sink for phosphate during most of the year, but under the reducing conditions caused by the decay of the organic matter accumulated during the summer, these complexes are released and sediments become a source of phosphate. For example, Manning (1977) measured that the upper 2 cm of sediments in the Bay of Quinte, a shallow eutrophic bay on the northern shore on Lake Ontario, released 50 to 150 g PO_4 m^{-2} in late August.

Mortimer's paradigm that oxygen controls the P release from sediments was widely accepted for many decades, but its universality has been questionned. Even though it has been successful at explaining internal loading when it occurs, it provides poor prediction of where and to what extent it will occur (Prairie et al., 2001). Many lakes do not follow the predictions of this model, such as lake 227 in the Experimental Lakes Area (ELA), where no bottom water P increase was observed under anoxic conditions, even under ice (Schindler, 1977). In contrast, some lakes experience internal loading even under oxic conditions such as Heney Lake (Southwestern Québec) (Carignan, 2003) and Lake Onondaga (New York state), where P release from sediments started five weeks before anoxia (Driscoll et al., 1993). In a study of North American lakes, Prairie et al. (2001) found that only two out of ten lakes followed the classic Mortimer model: all lakes exhibited a substantial release of iron from sediments at the onset of hypolimnetic anoxia, but Fe release was rarely associated with a synchronous P release. Thus, iron and phosphorus do not appear as strongly coupled as predicted by Mortimer's model.

Recent studies suggest a more complex mechanism for internal loading, involving a combination of biological and chemical processes rather than strictly chemical as suggested by the classic Mortimer model. Phosphorus release rates often exceed the amount of oxygen-controlled P loading (Hupfer et al., 2008). One proposed hypothesis include the existence of a different sediment P pool not bound to iron hydroxides but likely to organic matter (Boers & Van Hese, 1988; Sinke et al., 1990; Boers & De Bles 1991). Also, a high pH at the water-sediment interface decreases the P-binding capacity of iron and aluminium oxides, which might stimulate internal loading (Curtis, 1991). Conversely, a low pH induces the solubilisation of the settled calcite. This mineral also sorbs P, so its dissolution releases P back in the water column (Eckert et al., 1997). Other variables may explain P release from sediments such as temperature (Jensen & Andersen, 1992), the organic matter content in sediments (Reddy, 1983), and the fraction of P adsorbed to iron within the sediments (Nürnberg, 1988). Concentration of nitrates (Andersen, 1982), sulfates (Caraco et al., 1989) as well as calcium (Driscoll et al., 1993) could also play an important role in the P release dynamics.

These hypotheses have all been challenged and the exact mechanism of internal loading still needs to be elucidated. Prairie et al (2001) found that neither the composition of the sediments nor factors such as temperature, pH, calcium or nitrate concentration in the water could explain the differences in P release observed among ten North American lakes. The strongest predictor they identified was the oxygen consumption rate in the hypolimnion prior to anoxia, which suggests a dominating role of decomposition processes. In fact, between 10 and 75 percent of the potentially soluble sediment P is not likely sorbed to iron hydroxides but contained within microbial cells (Boström et al., 1988). Other processes influencing internal loading may include diffusion (Fisher et al., 2005), wind-wave generated sediment resuspension (Jin et al., 2007), bioturbation, and groundwater seepage (Pollman & James, 2011).

Bacteria consume oxygen during the degradation of organic matter and might store excess P under oxic conditions, and then release it during anoxic periods (Hupfer et al., 2007). Because microbial processes consume oxygen and release P, distinguishing whether oxygen depletion is the cause or the consequence of P release is difficult (Hupfer et al., 2008). Moreover, the oxygen penetration rate into sediments is very low, so only a small portion of the top sediments is oxic (Müller et al. 2003). As sediments accumulate over time, the once oxic sediments become anoxic and so iron oxides get reduced and the previously bound P is released back into the water column. In this sense, the hypolimnetic oxygen availability might control the dynamics of the short-term release of P, but not the long-term trends of internal loading (Hupfer et al., 2008). Nonetheless, the fact that internal loading often constitutes a major fraction of the P load to lakes during summer (Andersen, 1982) and can delay the recovery of lakes is well documented, and therefore remains a concern for the restoration of many lakes (e.g. Pollman & James, 2011).

Less than 20% of iron that accumulates in lake sediments eventually returns to the water column as ferrous iron (Davison & Tipping, 1984). A significant portion of iron is mineralized into the clay mineral chlorite during diagenesis (Davison & Dickson, 1984). This mineral is very stable so the iron it contains is not subject to further redox reactions. Inorganic sulfur also plays an important role in determining the iron solubility and cycling. During the oxidation of organic matter, sulfate (SO_4^{2-}) is reduced and the resulting hydrogen sulfide (HS^-) and sulfur (S^{2-})

combines with iron to form precipitates that are almost insoluble under anoxic conditions (Kalff, 2002). In lakes receiving a high Fe: SO_4 ratio from their catchment, when anoxic conditions develop, ferrous iron released from the sediments binds to H_2S and re-precipitates. These lakes allow high concentrations of dissolved iron in the anoxic hypolimnia. In lakes with low Fe: SO_4 ratio, such as carbonate-rich catchments, the majority of iron is precipitated as FeS and so little iron is available for P binding (Kalff, 2002). Such lakes may then be more prone to eutrophication.

1.1.3. History of eutrophication

Phosphorus and nitrogen were first identified as limiting nutrients in aquatic ecosystems by Atkins (1923) in England, Fischer (1924) in Germany, and Juday (1926) in the United States (Kalff, 2002). However, eutrophication only became a serious concern in the 1960s for lakes in North America and Western Europe. The main conclusions of a major international conference on this subject held in 1967 in Wisconsin were that nitrogen, and more importantly P, caused the summer algal blooms observed in previously oligotrophic lakes of temperate regions receiving wastewater and runoff from agricultural areas (Kalff, 2002). The following year, Vollenweider (1968, in Kalff, 2002) produced simple empirical models that associated P export from lake catchment to the in-lake TP concentrations and the phytoplankton biomass. Concomitantly, in the 1970s, dishwashers and washing machines became increasingly popular. Detergents for these appliances contained high amounts of P. Manufacturers first argued that it was not the P contained in their products that was increasing lentic primary production, but rather the CO_2 produced by the oxidation of organic matter in sewage systems. Schindler’s experiment (1974) on Lake 226 at ELA clearly demonstrated that P is the main limiting nutrient in freshwater ecosystems and that eutrophication remediation programs should focus on the reduction of this element.

Europe and North America have distinct histories of eutrophication. Europe has much higher current and historical population density than North America (Ramankutty & Foley, 1999); intense agriculture has also been part of Europe’s landscape for a much longer period (Ramankutty & Foley, 1999). In a review of 67 P reconstruction studies across North America and Europe, Keatly et al (2011) found that as early as ca. 1900, a higher proportion of European lakes compared to North American lakes were eutrophic or hypereutrophic. Also, 67% of European lakes exhibited a TP increase over the past 100 years, compared to 33% in North America. Interestingly, despite the efforts in reducing P inputs, no European lakes experienced a decrease in their total P concentration, while 31% of North American ones did. Carpenter (2005) suggested that long-term nutrient inputs to soils for agriculture could lead to over-enrichment of catchments and chronic internal loading. Because of the constant application of fertilizers over an extended period of time, soils accumulate P and continue to act as a nutrient source for many years after the application of fertilizers has ceased. For example, agricultural soil of the United States would accumulate P surpluses at a rate of about 22 kg/ha/yr mainly due to excess manure application (Carpenter et al., 1998). Lakes with a long history of extensive agriculture in their catchment could therefore respond more slowly to remediation techniques involving the reduction of external P sources.

Even though Keatley et al. (2011) found no evidence of change in TP concentrations in European lakes at a centennial scale through reconstruction methods, real-time monitoring data from the past 40 years do indicate that some lakes show signs of recovery. In a review of 35 case studies of lake "re-oligotrophication" in Europe, Jeppesen et al. (2005) found that reductions in P external loads lead to lower in-lake TP concentrations and chlorophyll *a*, and a greater transparency. The recovery time was dependant on internal loading processes and was faster with shorter hydraulic retention time; the majority of lakes reached a new equilibrium 10-15 years after the reduction of P inputs.

Some of the Great Lakes in Canada and the United States have been subject to serious water quality degradation. Lake Erie was recognized as undergoing cultural eutrophication in the early 1960s. Beeton (1960) reported decreasing levels of dissolved oxygen since the 1930s, a shift in the bottom fauna with commercial fish species becoming more scarce, and increasing temperatures. A massive algal bloom in July 1970 led to the deposition of a 2 to 3 cm-thick layer of algae on the lake floor (Burns & Ross, 1972). The subsequent algal decomposition decreased oxygen levels and induced important phosphate releases from the sediments. A second massive bloom occurred in September as the surface waters mixed with the underlying phosphate-rich waters. The increasing human population and sewage introduction in the ~100 years prior to

Beeton's study likely increased the nutrients input. Improved knowledge about eutrophication processes, particularly Schindler's experiment in the ELA (1974), led to basin-wide reduction of point source nutrient inputs in the Great Lakes during the 1970s, and a subsequent reduction of phytoplankton biomass. Despite these efforts, a resurgence of algal blooms has been observed since the 1990s, in the Great Lakes as well as in other lakes in Ontario and Québec (Medeiros & Molot, 2006). Today, eutrophication of lakes, rivers and coastal areas remains a major concern and many remediation programs are in progress with the goal of mitigating eutrophication and protecting water resources (Jeppesen et al, 2005). Reducing external nutrient loading has also been combined with restoration methods including biomanipulation (Benndorf, 1990) and physico-chemical methods (e.g. Cooke et al., 1993).

1.2. Paleolimnology

1.2.1. Definition and applications

Freshwater ecosystems have been subject to anthropogenic pressure for the last ~150 years in North America (e.g. Vermaire et al, 2012). In order to determine whether environmental changes have occurred or not in lakes and rivers, pre-existing conditions before the stress induced by human activity need to be elucidated. However, for the majority of North American lakes, long-term monitoring of limnological conditions does not exist and so other tools are needed to determine if changes in environmental conditions have occurred. Such information is relevant to better understand how ecosystems change over time, but also to inform decision-makers and lake-management communities about the historical patterns and causes of nutrient loading (Cohen, 2003).

Paleolimnology is a multidisciplinary science aiming to reconstruct past environmental conditions, using physical, chemical and biological information preserved in sediments (Smol, 2008). Every year, sediments accumulate at the bottom of lakes and contain the remains of organisms that were once living in that water body such as algae, plants or fish, as well as allochtonous material like tree pollen. The sediments in the deepest area of a lake integrate the aquatic community that inhabited the lake at the time of deposition (Smol, 2008). Therefore, the top portion of sediments reflects the biological diversity currently inhabiting the lake. By combining the information on the biological community in a water body with its geochemical conditions, one can associate the distribution of organisms and the environmental conditions in which they live. As a result, the analysis of fossil community assemblages in a sediment core, used in conjunction with the species' environmental optima and tolerance data, can yield information about the past conditions in individual lakes.

1.2.2. Inference models and training set - transfer functions

The method used to infer paleolimnological conditions is a training set – transfer function approach, in which the known present-day ecology of organisms is used to infer the past environmental conditions. This approach holds on the central tenet in ecology that the distribution and abundance of organisms are mainly controlled by chemical, biological and physical environmental constraints (Smol, 2008). In order to build a transfer function, the first step is to choose a suite of reference lakes, or "calibration" lakes, which span the environmental conditions one is interested in and that are likely encountered in the limnological history of the lake of interest. Therefore, the majority of taxa in the sediment core from the lake of interest should be found in the reference lakes. Then, the surface sediments, usually the top centimeter, are collected at the deepest location of each of the reference lakes in its deepest area, where most sediment accumulate due to sediment focusing processes. A long sediment core is also retrieved from the deepest area of the lake of interest. A first matrix is built containing the environmental conditions in each lake. The identification and enumeration of biological indicators found in the surface sediment in each lake is then used to build a second matrix. The transfer function is finally developed using statistical techniques and is used to reconstruct the past environmental conditions of the lake of interest by comparing the calibration data set with the fossil assemblage at the different depths of its sediment core (Smol, 2008; Cohen, 2003). This core should also be dated using radioisotopic techniques such as lead-210 or radiocarbon. The training set - transfer function is a well-established and widely-used technique and is considered the most powerful way to relate distribution and abundances of taxa to past environmental variables (Smol, 2008).

Many organisms can be used to build transfer functions in order to infer past environmental conditions. A good paleoecological proxy meets certain criteria: good preservation in the sediments, niche-specificity, relatively fast response to changing environmental conditions, and relative ease of identification. The choice of the paleoecological proxy more importantly depends on the research question and the environmental variable one is interested in. Examples of biological paleoecological proxies include pollen, plant macrofossils, chrysophyte scales and cysts, chironomids, and the most commonly used, diatoms (Bacillariophyceae) (Kalff, 2002).

1.2.3. Diatoms as paleoindicators

Diatoms are an important group of algae in freshwater temperate systems, where they typically contribute to over half of the aquatic primary production (Smol, 2008). These microscopic algae are unicellular, though some species form colonies. They produce a siliceous cell wall called the frustule, composed of two interlocked theca (the hypotheca and the epitheca), or valves. The taxonomy is primarily based on the sculpturing of these valves, as well as their shape and size. To date, the number of species described is ~ 30,000 but there could be as many as 100,000 species (Mann & Vanormelingen, 2013). Diatoms are certainly the single most valuable group of fossil organisms for paleolimnological reconstruction for multiple reasons (Cohen, 2003). Their siliceous frustules allow for excellent preservation in sediments as they resist physical breakage, bacterial decomposition and chemical dissolution. Diatoms live in a wide range of environments including oceans, lakes, rivers, streams and wetlands. Because of their sensitivity to limnological conditions and their fast migration and reproduction rates, their species assemblage closely tracks environmental shifts with minimal lag times (Cohen, 2003).

Bacillariophyceae have been used to develop inference models for the reconstruction of a variety of variables including pH, salinity, alkalinity, stratification, and nutrient availability (e.g. Cohen, 2003; Tremblay et al, 2014). Nutrient availability in aquatic systems is important for structuring algal communities (Cohen, 2003) and different diatoms species have particular P and silica (Si) requirements (e.g. Hall & Smol, 1999). Determination of the various diatoms species optima and tolerance ranges for particular nutrients allows the development of inference models (Tremblay et al, 2014) and the methodology for developing these is well documented (e.g. Birks 1995, Birks et al, 2012).

Diatom training sets and inference models are very useful in reconstructing past nutrient conditions and yield better tracking of eutrophication periods than the simple measurement of changes in sediment P levels because of the mobility and diagenetic complexity of this element (Anderson & Rippey, 1994). Hall and Smol (1992) were the first to use the transfer function approach to infer total P concentrations from fossil diatom assemblages and since then, many other inference models have been developed for numerous regions and variables (Smol & Stoermer, 2010). However, this approach has its limitations. For one, it depends on the assumption that the modern training-set taxa are the same biological entities as in the fossil record and that their ecological response to changes in environmental conditions has remained constant over time. Also, the use of a training set – transfer function is restricted to its region of origin as comparison between different models show poor spatial replicability (Juggins 2013; Telford & Birks, 2009). As an example, some training sets exist in the province of Québec (Canada), but they are based on lakes in the Eastern townships, the Laurentians (Tremblay et al., 2014) and Abitibi Témiscamingue regions (Enache & Prairie, 2002; Philibert & Prairie, 2002) regions. No training set specific to the Outaouais region is currently available.

1.3. Objectives

This thesis tests the general hypothesis that Canadian Shield lakes with more carbonate bedrock (e.g. marble) in their catchment are more prone to iron deficiency. This in turn makes such lakes more susceptible to cultural eutrophication than lakes on entirely granitic bedrock. Under conditions of low iron concentration, P is less prone to precipitation and accumulation in sediments.

The first objective was to determine whether iron deficiency in the plankton is a function of the extent of carbonate rock in the catchment of lakes of the Outaouais region of Southwestern Québec. This region encompasses a range of bedrock types and land use. Some of its numerous lakes have also experienced algal blooms in recent years (Leblanc et al., 2008) despite low population densities and little farming activity. I hypothesize that some lakes, particularly those with marble or other carbonate rocks in their catchment, may be more susceptible to eutrophication.

The second objective was to reconstruct the history of one of the Outaouais lakes that has undergone significant cultural eutrophication with the goal of establishing a realistic nutrient mitigation target. Heney Lake experienced a period of eutrophication stemming from a fish farm operation. As the lake was deemed iron deficient, a large-scale iron chloride addition was implemented to reduce the lake phosphorus concentration, and hence control algal biomass. However, the target P levels for remediation were not based on information on pre-European settlement conditions such that the current targets may be either unrealistic or not sufficiently ambitious. Determining the pre-settlement trophic conditions is critical as residents and regional authorities wish to restore the lake.

These two objectives are addressed in two chapters, written as individual articles. Chapter 2 provides an overview of the geochemistry of the lakes in the Outaouais region, with an emphasis on the degree of iron deficiency in relation to the watershed bedrock composition, as well as iron-phosphorus interactions. Despite the proximity of these lakes to the national capital of Canada, their limnological conditions are largely unknown. These lakes then served as the training set for the paleo-reconstruction of one of these lakes. Chapter 3 aims at establishing the history of Heney Lake in terms of productivity and nutrient status, focusing on the last ~200 years which corresponds to the European settlement of this area.

1.4. Lakes of the Outaouais region, Québec

Europeans colonized the Outaouais region during the XIXth century (NCC, 2005). The city of Hull was founded by Philemon Wright in 1800 with the intention of developing agriculture in the area (Sabourin, 2010). Farmers quickly realized the soil was not very fertile and so logging rapidly became the main economic activity; within less than 40 years Hull and the surrounding region became an important wood producer for the colony (Sabourin, 2010). Many rivers, including the Ottawa River, the Gatineau, the Noire and the Coulonge were used for the transportation of logs until the second half of the XXth century. Today, the economic development of the rural Outaouais region remains logging and the pulp and paper industry, with some pasture and forage crops. Many recreational homes have been built along Outaouais lakes and river shores. Nevertheless, a large portion of the region remains forested.

The Outaouais region, like much of Québec, Ontario, Saskatchewan, Manitoba, Northwest Territories and Nunavut, is on the Canadian Shield. The little remaining part belongs to the

St. Lawrence Lowland. The Canadian Shield is the largest mass of exposed Precambrian rock on Earth with ~ 4 million square kilometres of rocks that are 0.5 to 4 billion years old (Bastedo, 2006). The majority of the Canadian Shield is composed of granite (Rock Ontario, 1994). However, a portion of the Shield contains calcitic and dolomitic marble, as well as metamorphosed gneiss. Younger intrusive plutonic rocks such as diorite, gabbro and syenite are also present. The Canadian Shield was subject to a long history of orogeny, uplifts and depressions, and erosion (Encyclopædia Britannica, 2015). Major orogenic events during the Middle Proterozoic 1600 – 900 Ma led to a large mountain chain with peaks ~12,000 meters high (Gall, 2010). Thousands of years of erosions flattened the landscape subsequently. Repeated advances and retreats of continental ice shelves during the Paleozoic and Cenozoic era have scoured, scraped and gouged the hard bedrock, leaving millions of shallow basins that filled with water to become lakes, rivers, streams and wetlands (Bastedo, 2006). As they retreated, the ice sheets deposited the sand, gravel and clay they carried, which dammed up rivers. As a result, water bodies were forced to flow in different directions, leading to disorganized patterns of winding rivers and streams.

The Outaouais region counts more than 15,000 lakes (Government of Québec, 2002) and covers 30 472 km^2 with a population density of 1.1 inhabitant/km^2 (Governement of Québec, Institut de la Statistique Québec, 2014). Water quality of these lakes is generally good (Santé Publique Québec, 2008), but they are not sheltered from the numerous anthropogenic stresses that affect many lakes on the Shield such as logging, agriculture, hydroelectric dams, water level controls, non-indigenous and invasive species as well as housing development (Yan et al., 2008). An increasing number of cottages and houses are being built along lakes' shores, which implies tree cutting, landscape modifications, application of P-rich fertilizers to lawns and hobby farms, increased nutrient inputs to lake, as well as possible leaks from septic tanks. One of the study lakes of this thesis is Heney Lake, which in addition to the above development pressures experienced that of a fish farm, which led to significant nutrient loading to the lake.

Lake Heney is located on the Canadian Shield and is administratively shared between the municipalities of Gracefield and Lac Sainte-Marie in the *MRC de la Vallée de la Gatineau*, in Western Québec (45º 59' N, 75º 55' W). Unlike the majority of lakes of the Precambrian Shield, Lake Heney and half of its watershed lies on calcitic and dolomitic marble, which have a low concentration of certain minerals including iron, aluminum and sulphur (Carignan, 2003). This particular bedrock composition yields a water chemistry characterized by relatively high calcium and magnesium concentrations (10-30 mg/L and 1-3 mg/L, respectively), as well as a slightly alkaline pH (7-9).

Lake Heney's watershed is 78.6 km^2, of which 95% is covered with 40-100 year old deciduous forest (Carignan, 2005). The rest of the catchment consists of deforested land, mainly dedicated to forage crop and pasture (Carignan, 2003). There are five fishing and hunting outfitters as well as a sawmill (FONDEX Outaouais, 2005). The lake's shape is elongated in a north-south axis and covers over 12 km^2, with 32.6 km of shoreline along which about 300 residents live, including permanent residences as well as seasonal cottages. From 1994 to 1999, a fish farm raised trout in Whitefish Bay, in the North-East portion of the lake. Since the beginning of the fish farming activities, residents noticed a degradation of the water quality. In order to protect the lake from more serious degradation, the Association for the Protection of Lake Heney (APLH) filed a class action against both the private company that operated the fish farm, Truiticulture S.L., and the MDDELCC (Ministère du Développement Durable, Environnement et Lutte contre les Changements Climatiques). In 1999, the APLH won its case with a large monetary settlement for restoration; the courts forced Truiticulture S.L. to stop its activities.

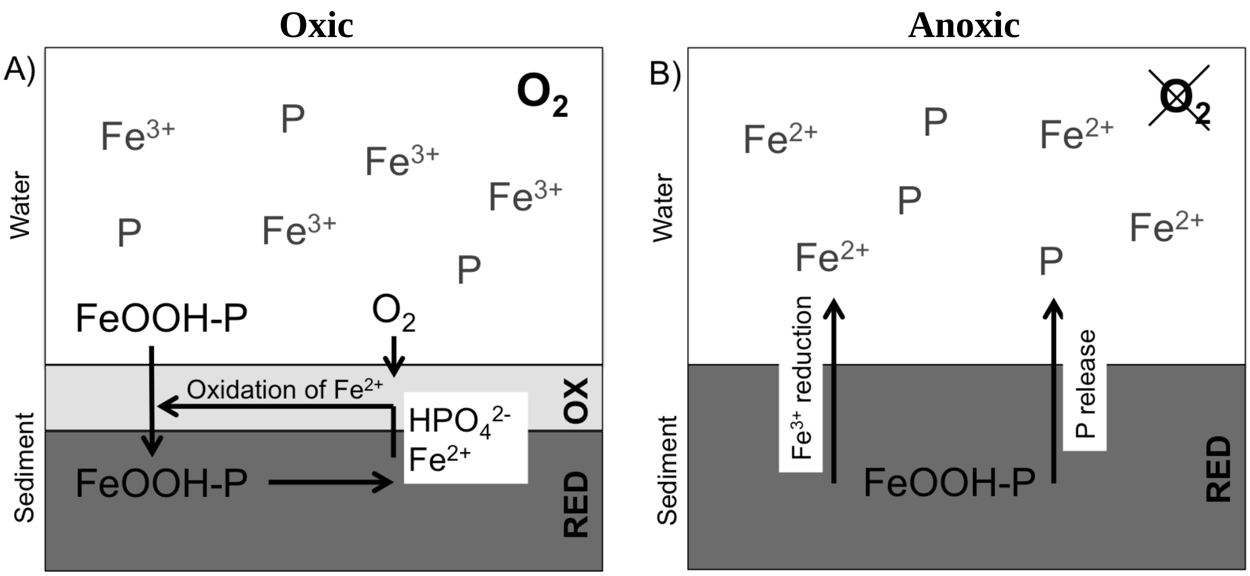

Figure 1 Coupling of iron and phosphorus cycle at the sediment-water interface in A) oxic hypolimnion and B) anoxic hypolimnion, based on the classical studies of Einsele (1936) and Mortimer (1942). OX – oxidized sediment layer; RED – reduced sediment layer; FeOOH~P – phosphorus bound to Fe(oxy)hydroxides. Modified from Hupfer et al. (2008).

2. The geochemistry of lakes in the Outaouais region, Québec, with a focus on iron and phosphorus

2.1. Introduction

Lakes are a reflection of the ecoregion in which they lie as well as their drainage basin proprieties such as topography, geology, land use, vegetation cover and soil characteristics (Kratz et al., 1997). Typically, a high catchment area to lake area ratio (CA: LA) offers more time and space to collect precipitation and nutrients from the soil and bedrock weathering. As a result, lakes with large CA: LA ratios receive significant quantities of nutrients through surface runoff and tend to have relatively high nutrient concentrations and high algal productivity (Kalff, 2002). In contrast, lakes with small CA: LA ratios obtain a significant portion of their nutrients from atmospheric loading, which yields lower nutrient and dissolved salt concentrations. These lakes are also typically located higher in the landscape, in the upper subcatchment portions of large catchment systems (Kalff, 2002). Yong and Harvey (1992) suggested that catchment-driven processes control Fe inputs and accumulation in sediments rather than in-lake processes. The CA: LA and other catchment properties could therefore be important in determining the relative abundance of Fe in lake water.

Because the vast majority of micro and macronutrients and other elements inputs to lakes and rivers come from the soil and bedrock weathering (Likens et al., 1977), the geological setting of lakes and their catchment plays an important role in determining the water chemistry. For example, the vulnerability of lakes to acidification is largely a function of bedrock geology (e.g. Driscoll et al., 2001). In the case of eutrophication, Reynolds and Petersen (2000) found that lakes in Ca-rich catchments were more susceptible to cyanobacterial blooms. Calcium is a macronutrient that is required, to varying degrees, by all living organisms and the main Ca reservoir for a lake is its catchment bedrock and soil (Smol, 2010). Similarly, because of the importance of Fe in sequestering P in lakes sediments, lakes located on bedrock geologies with low Fe may be more susceptible to eutrophication in the case of increases in P loading.
In a study of 208 temperate lakes, Duarte and Kalff (1989) observed that catchment geology and mean depth of the lake described the variability in algal biomass almost as well as did the in-lake TP concentration. Phosphorus-rich sedimentary rocks such as limestone and mudstone typically increase the P iutputs to freshwaters, compared to P-poor igneous rocks such as granite.

In addition to catchment geology, land use has major impacts on the trophic status of lakes (e.g. Gergel et al., 1999). The supply rate of elements from the surface runoff in the catchment depends on the land use and the requirements of land vegetation. As a result, the proportion of a particular type of land cover or land use within a catchment has been used to explain, predict and model water chemistry (e.g. Hunsaker & Levine, 1995; Johnson et al., 1997), algal abundance (Richards & Host, 1994), aquatic invertebrate community composition (Barton, 1996) and biotic integrity of fish communities (Allan et al., 1997). Elements that are in higher demand by terrestrial vegetation, mainly phosphorus, nitrogen and potassium, are retained on land rather than exported to outflowing streams (Kalff, 2002). Elements that are in relatively low biological demand such as calcium, magnesium and sodium, are in contrast more readily transported to streams. Over an 11-year study in the undisturbed forest ecosystem of the Hubbard Brook drainage basin (Massachusetts), Likens et al. (1977) found that <1 % of the P reaching the forest floor was lost through stream water output. The rest of the P was incorporated into vegetation at 82 %, while 18% was incorporated into the forest floor.

Additionally, the hydrological connectivity of lakes with other surface water features may be important for lake water chemistry; water drainage does not necessarily track bedrock geology as inflowing waters are typically channelized. The lake nutrient response to intensive agriculture in the catchment, as well as lake organic carbon in relation to the wetland cover in the catchment differs among lakes with different connection strength and patterns to rivers and streams (Soranno et al., 2010). In a lake chain setting, the headwater lake can be a source of N and a sink of P, while the lakes downstream are a source of both these nutrients, as observed in the North American Rockies (Epstein et al., 2013). Also, there is growing evidence that both the lake nutrient concentration and the relationship between land use and lake nutrients vary regionally depending on the local hydrogeomorphic setting, defined by features including climate, topography and hydrogeology (Winter, 2001). The relationships between in-lake nutrient concentrations and intensive agriculture in the catchment, as well as lake organic carbon and wetland cover in the catchment have been found to differ among lakes with different connection strength and patterns to rivers and streams (Soranno et al., 2010; Gergel et al., 1999). In a study of 146 north temperate lakes, Soranno et al. (2015) found that lake hydrologic connectivity, region and spatial extent of land use measurements influenced land use – lake nutrient relationships, with lake hydrological connectivity having the most important effect. The authors classified the lakes into three categories of hydrologic connectivity: isolated lakes (no connectivity to streams or other lakes), drainage lakes with stream inflows (fed by inflowing streams or rivers) and drainage lakes with streams and lakes (at least one lake in their catchment) and found that nutrient concentrations were not significantly different between categories, but that the lake hydrologic classes were functionally different in their response to external drivers.

Human activity through changes in land use can alter the export of nutrients to lakes and rivers (Soranno et al., 2015). In agricultural areas for example, nutrient retention is much lower as the supply exceeds the demand by the biota due to the use of P and N fertilizers (Kalff, 2002). Deforestation decreases the P and N demand on land and leads to increased export to aquatic ecosystems. Dillon and Kirchner (1975) found that for drainage basins on igneous bedrock of the Canadian Shield in Ontario, a change in land use from forested to a combination of forested and pasture doubled the amount of P export. The effect of land use change had a similar impact in a sedimentary bedrock setting south of the Shield. However, the P export from a P-rich sedimentary rock watershed was twice the export from an igneous watershed. It also appears that the combination of land use change (forested to forested and pasture) with bedrock type (igneous or sedimentary) have a multiplicative effect on the P export rather than additive.

A majority of the Canadian Shield is composed of igneous rocks such as granite and syenite, which contain relatively high amounts of iron and other accessory minerals and low phosphorus (Carignan, 2003). However, lenses of marble and other carbonate rocks are present in the Southern part of the Shield, near Ottawa (SIGEOM, 2015). These typically have low concentrations of accessory minerals like iron (Carignan, 2003). Low iron concentrations may in turn lead to a lack of P sedimentation and hence modify the P cycle of such lakes.

I hypothesized that certain lakes of the Canadian Shield, more specifically those that have a watershed lying on carbonate bedrock such as marble, may exhibit a relatively greater iron deficiency and therefore, could be more susceptible to eutrophication. To test this hypothesis, I selected of suite of 31 lakes in the Outaouais region, southwestern Québec, that span a range of geological settings and land use. The geochemistry of lakes in this region has not been extensively studied. Yet, these lakes, given their proximity to a growing urban centre (Ottawa-Gatineau), will likely experience future development pressures. Considering the large number of lakes in Canada, there is a need to develop tools to assist in predicting which lake types may be more prone to eutrophication.

2.2. Materials and methods

2.2.1. Study lakes

A total of 31 lakes in the Outaouais region (southwestern Québec) on the Canadian Shield were chosen based on a range of land uses and across a variety of geological units (Fig. 2.4). Regional land use was determined with satellite images from Google Earth and geological units were identified with the *Système d'Information Géominière du Québec* (SIGEOM). The bedrock of lakes and their watershed consists mainly of granite and syenite, as well as gneisses and calcitic and dolomitic marble (Gall, 2010), locally overlaid by thin glacial deposits of the Wisconsinan glaciation 80 to 12 thousand years BP (Richmond & Fullerton, 1986). As a result it was anticipated that the lakes would range in geochemical and trophic conditions, mainly total phosphorus, iron and calcium. Most of the lakes' shore and watershed are covered with temperate mixed forest, as indicated by satellite images and field observation, but some small-scale forage crop and pasture activity are locally present. Some lakes, such as Lake Heney, have as many as 350 houses and cottages along the shoreline, while some lakes had no visible trace of human activity. The majority of lakes are used for recreational purposes such as boating, fishing and swimming.

2.2.1. Geological and morphometric variables

Lake perimeter, size and watershed area were determined with ArcMap® software using Digital Elevation Maps (DEM) obtained from the U.S. Geological Survey, and hydrology shapefiles from DMTI Spatial inc. available on Scholars Geoportal's website. The watersheds of the selected lakes were determined using the *Batch Watershed Delineation for Polygons* in the *Arc Hydro Tools* toolbox. With detailed bedrock geology shapefiles from the *Système d'Information Géominière du Québec (SIGEOM)*, *Ministère de l'Énergie et Ressources Naturelles Québec*, the

Clip tool was used to determine the relative bedrock composition of each watershed. The number of houses and cottages were counted using satellite images on Google Earth®. The number of houses was then divided by the lake perimeter in order to obtain house density. Lakes were also classified as drainage lakes or isolated lakes. Using each lake's watershed map produced in ArcMap, lakes that had no other lakes > 5 hectares in their catchment were classified as isolated lakes while lakes with other lakes in their catchment were classified as drainage lakes.

2.2.2. Water and sediment sampling

Sampling of the 31 lakes occurred between September 2013 and July 2014. Sampling sites are shown in figure 2.4. Each lake was visited once and a depth sounder mounted on a canoe was used to find the deepest location. A GPS (Magellan Triton 400) was used to record the coordinates and the following variables were measured *in situ* with a Hydrolab Minisonde 5 connected to a Hydrolab Surveyor 4: temperature, dissolved oxygen (DO), pH, oxidation-reduction potential (ORP) and conductivity. These variables were recorded at 0.5 m intervals in the epilimnion and metalimnion and at 1 m intervals in the hypolimnion. Dissolved oxygen was calibrated before every field trip while pH, ORP and conductivity were calibrated on a monthly basis. Secchi depth was also measured for an estimate of the depth of the photic zone. In each lake, six litres of subsurface water were collected in 2L polypropylene Nalgene® bottles rinsed three times with lake water and kept in a cooler until analysis. Three to five sediment cores were retrieved from the deepest part of the lake using a Glew Gravity corer. All cores were extruded in 0.5 cm subsections and the top 2 cm of sediments were collected in Whirlpacks or Ziploc Freezer bags and stored at -18ºC until analysis.

2.2.3. Water, seston and sediment chemistry

Whole lake water was analysed at the City of Ottawa Water Laboratory Services for total phosphorus (TP), total Kjeldhal nitrogen (TKN), major cations (e.g. Ca, Mg) using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and dissolved metals (e.g. Fe) using Inductively Coupled Mass Spectrometry (ICP-MS). Aliquots of lake water (2 x 300 ml) were filtered through 1.5 μm glass fibre filters (934-AH, Whatman) for planktonic chlorophyll *a* as an estimate of algal biomass. Filters were then frozen at -18ºC until pigment extraction.

Chlorophyll *a* was extracted by immersing each filter in 15 ml of 95% ethanol for 24 hours at 4ºC (Jespersen & Christoffersen, 1987) and concentrations were estimated using a Varian Cary® 100 BIO UV-visible spectrophotometer. Alkalinity was determined by titration using 1N HCl solution following standard methods (APHA, 1982).

In order to determine the particulate iron (Fe part) and phosphorus (P part) concentrations as an index of their relative concentrations in the plankton, 500 to 1500 ml of lake water were filtered through 1.2 µm glass fibre filters (Whatman GF/C) within 12 hours after sampling then stored at -18ºC until analysis. Filters were dried at room temperature overnight then at 80ºC for two hours. Acid digestion of filters was done in a DigiPrep heating block according to DigiPrep (SCP Science) protocols following USEPA method 200.2 (EPA, 1994) and digested with metal grade nitric acid at 95ºC for three hours. The samples were then analysed using an Agilent 7700x ICP-MS. All glassware was acid-washed overnight using a 5% HCl solution. Surficial sediment samples were freeze-dried overnight, then digested with metal grade nitric acid at 95ºC for three hours. Following filtration with 0.45 µm teflon membrane (DigiFILTER), samples were analysed using an Agilent 7700x ICP-MS. To measure the background concentrations, blank filters were used as controls on ultrapure water (Milli-Q® integral water purification system) and were subjected to the same procedure as lake samples. Three samples of the standard NIST 1515 (apple leaves) were prepared following the same method as the lake samples to validate the methodology and assess the recovery rates.

Loss on ignition (LOI) at 550ºC following Heiri et al. (2001) were performed on the surficial sediments to assess the organic carbon content. The combustion was done on the same samples used for ^{210}Pb dating. Samples were dried at 105ºC overnight, weighed with a Mettler Toledo XS205 Dual Range scale and ashed in a muffle furnace at 550ºC for 4 hours, with an 8 hours gradual warm-up phase, and weighed again. The weight loss is proportional to the amount of organic carbon in the sample (Dean, 1974; Heiri et al., 2001). The following equation was used to determine the LOI at 550ºC, expressed in percentages.

$LOI_{550} = ((DW_{105} – DW_{550})/DW_{105})*100$

where DW_{105} is the dry weight of the sample before combustion, DW_{550} the dry weight of the sample after heating to 550ºC.

2.2.4. Statistical analysis

A multiple linear regression analysis was performed using the R® software (R Development Core Team, 2013) in order to test for the anticipated relationships between water and sediment chemistry and catchment characteristics. Six lakes had a TP value below the detection limit were therefore attributed a value between 0 and the detection limit through a random number generator. Most variables were transformed to obtain a normal distribution (Shapiro-Wilk test). The following variables were log-transformed: Elevation, SA, CA, TP_p, Fe_p, Fe_TP_p, TP, TKN, Cal, Fe_d, Chl, Cond, Sec, Fe_TP_w, TP_s (see Table 2.1 and 2.2 for variable names), while a square root transformation was applied to: MD, HD, MP, CP, Fe_s, Fe_TP_s. One variable had the transformation ^2 (pH) and one variable had a 1/square root transformation (CA_SA). Some variables were normally distributed without any transformation and remained untransformed for the statistical analyses (HD, Alk, Fe_TP_s, LOI). The same transformations were applied for the calculation of the Pearson's correlation matrix. The variable conductivity was deleted for the analysis as it was collinear with calcium. Also, epilimnetic dissolved oxygen was dropped as the variations in the readings were most likely due to the time of the day at which we sampled, as this variable varies greatly throughout the day. A backward stepwise approach was used to find the best model and for each term dropped, an ANOVA was performed to compare the longer model with the shorter model. If the difference between the two models was not significant, the simpler model was retained. Moreover, only variables with an associated p-value < 0.05 were retained. All selected models were tested for assumptions using: Breusch-Pagan (homoscedasticity), Durbin-Watson (autocorrelation), Reset test (linearity) and Shapiro (normal distribution). Also, visual inspection of the graphs: residuals vs. fitted, Normal Q-Q plot, Scale-Location and Residuals vs. Leverage were performed to test assumptions, as VIF values were calculated for multicollinearity.

2.3. Results

Basin characteristics

The set of lakes encompassed a wide range of basin features. Lake area varied from three hectares (Kalalla) to 1231 hectares (Heney) (Table 2.1). The catchment area to surface area ratio

(CA: SA) also varied with some catchments only two to three times the size of the lake itself (Bataille, Truite) while other catchments were 150 times the size of the lake (Trois Monts, Guilbeault). At the time of sampling, all lakes were stratified except lac des Vases because of its shallow depth (1 m). All the other lakes were deeper, ranging between 4 m (Létourneau) and 53 m (Bataille). The geological setting varied among sampled lakes: some lake catchments were entirely composed of marble (Orignal, Truite) while others were entirely underlain by non-carbonate rock such as gneiss, syenite and granite (Bataille, Jean Venne, Pink, Renaud).
In terms of human development, a majority of lakes had a limited number of residential buildings, including summer houses and permanent residences. Only Pink lake and Lac à la Truite had no buildings along the shoreline. Some lakes are protected as they belong to the Gatineau Park (Pink, La Pêche and Renaud). The most developed lakes were Lac des Loups and Lac Fraser, both with a house density of 16 houses/km of shoreline (Appendix I).

Predicting water chemistry from basin features

Calcium and related variables

As anticipated, the study lakes spanned a range of calcium concentrations (Table 2.1, Appendix I). Lakes with very low Ca, and hence more typical of softwater Shield lakes include lakes Jean Venne, Renaud, Profond and Bonin. Lakes with high Ca, typically associated with sedimentary or certain metamorphic bedrock, include Pink, Bob, Demi-Lune, and Kalalla. Given the presence of marble in the region, I hypothesized that this variable would explain calcium concentrations in surface waters as well as limnological variables typically associated with calcium (conductivity, alkalinity, and pH). This hypothesis was supported by the positive correlations between percent marble and these variables (Appendix II), but these were not significant when Bonferroni-adjusted. A multiple regression analysis of calcium concentrations based on the basin features (Table 2.1) retained percent marble as the only significant independent variable, explaining 12% of the variation in caclium concentrations (model 1).

(1) $\text{Log(Cal)} = 1.17(\pm 0.06) + 0.03(\pm 0.01)\ \text{sqrt(MP)}$ $(r^2_{adj} = 0.12)$ $(p < 0.05)$

As anticipated conductivity, pH and alkalinity were all significantly correlated with Ca (Fig. 2.1, Appendix II). These parameters were also correlated with the percent marble in the catchment, but not significantly when Bonferroni adjusted (Fig. 2.1, Fig. 2.2 A, Appendix II). Not surprisingly, the models for pH, alkalinity and conductivity were similar (Appendix III). In a stepwise multiple regression analysis, the percent marble was the only independent variable retained for the prediction of alkalinity and conductivity (Appendix III models 8, 9). As for the pH model, the catchement area to lake surface area ratio was also retained as a significant variable. A higher proportion of the variance of pH ($r^2 = 0.31$) was explained with basin characteristics than for alkalinity and conductivity ($r^2 = 0.26$ and $r^2 = 0.12$, respectively).

(2) (pH)^2 = 54.71(±2.54) + 1.25(±0.31) sqrt(MP) ($r^2_{adj} = 0.31$)
+ 16.21(±5.95) 1/sqrt(CA_SA) ($r^2_{adj} = 0.44$)
($p < 0.01$)

Similarly to model 1, percent marble was the most important predictor and explained 31% of the variance in pH. This variable was positively correlated with pH (Fig. 2.1), therefore lakes with a higher proportion of marble in their catchment had more alkaline surface waters. The catchment area to surface area ratio explained an additional 13% of the variance in pH. Although this term had a positive slope in model 2 and was positively correlated with pH (Fig. 2.1), the relationship between pH and CA: SA is negative because the transformation applied to the latter variable is the reciprocal of its square root. Therefore, lakes with a higher catchment area to lake area had lower pH values.

Macronutrients and iron

The set of lakes spanned an order of magnitude variation in total phosphorus (Table 2.1). Based on TP, TKN, Secchi depth and chlorophyll *a* (Table 2.1, Table 2.2), the majority of lakes were oligotrophic (Kalff, 2002), with a few mesotrophic ones (Noir, Heney and Guilbeault). As often found in other lake studies, these variables were strongly correlated with one another (Fig. 2.1). The average mass TKN: TP ratio was 56, with a minimum of 25 (Lac Noir) and a maximum of 144 (Lac Jean Venne). As a mass TN: TP ratio above 17 indicates P limitation (Hellström, 1996), this suggests all the study lakes were P-limited (Appendix I).

Basin features allowed for prediction of TP with stronger explanatory power than the model for Ca. However, in the case of TP, maximum depth and the density of housing around the lake were the main predictor variables (model 3), as opposed to percent marble and surface area for the Ca model.

$$(3)\ \log(TP) = 0.87(\pm 0.11) - 0.08(\pm 0.03)\,\mathrm{sqrt}(MD) \qquad r^2_{adj} = 0.11$$
$$+\ 0.10(\pm 0.04)\,\mathrm{sqrt}(HD) \qquad r^2_{adj} = 0.25$$
$$(p < 0.01)$$

The most important independent variable in model 3 was lake maximum depth, with a negative slope, meaning that deeper lakes had less TP, which was confirmed with the negative correlation in the Pearson's correlation matrix (Fig. 2.1). House density was not significantly correlated with TP (Appendix II) however when the effect of maximum depth was controlled for in the linear model, house density was significant and explained an additional 14% of the variation in TP. Lakes with higher shore housing density therefore exhibited higher TP concentrations. Overall, these two basin features explained 25% of the variance in TP in the study lakes.

The iron concentrations in the study lakes varied over two orders of magnitude from the detection limit to over 100 µg/L (Appendix I). The only catchment property that had a significant effect on the dissolved iron concentration in lake water was the catchment area: lake surface area ratio. As the catchment area increases in proportion with the lake surface area, the dissolved iron concentrations increase as well.

$$(4)\ \mathrm{Log}(Fe\_d) = 1.46\ (\pm 0.20) - 1.94\ (\pm 0.54)\ 1/\mathrm{sqrt}\ (CA\_SA) \qquad r^2_{adj} = 0.29$$

In order to test the hypothesis that lakes with a high proportion of marble in their catchment would be more prone to iron deficiency, I analyzed both the ratio of iron to phosphorus in water as well as that in the seston since the latter provides a more direct estimate of the iron status of the plankton. Lakes with lower Fe: TP in the seston were assumed to be more prone to iron deficiency than lakes with high ratios. The Fe: TP ratio in the seston correlated significantly with the Fe: TP measured in the water (Fig. 2.1, Fig. 2.2 C, Appendix II).

Similarly to model 4, the only basin characteristic retained in the model of Fe: TP in water was the catchment to surface area ratio (model 5 *a*).

$$(5\ a)\ \mathrm{Log(Fe\_TP\_w)} = 0.53(\pm 0.22) - 1.49(\pm 0.60)\ 1/\mathrm{sqrt(CA\_SA)} \qquad r^2_{adj} = 0.14\ (p < 0.05)$$

With increasing CA: SA ratio, the Fe: TP increases as well. Although significant, the model only explained 14 % of the variation in the water Fe: TP ratio. However when other water chemistry variables were included as independent variables, calcium was also retained (model 5 *b*).

$$(5\ b)\ \mathrm{Log(Fe\_TP\_w)} = 2.13(\pm 0.61) - 1.26(\pm 0.45)\ \log(\mathrm{Cal}) \qquad r^2_{adj} = 0.17$$

$$- 1.41(\pm 0.54)\ 1/\mathrm{sqrt(CA\_SA)} \qquad r^2_{adj} = 0.31\ (p < 0.01)$$

Calcium concentrations and the CA: SA ratio were both individually correlated with water Fe: TP ratio (Appendix II). In the stepwise multiple regression, calcium was the first independent variable retained and predicted 17% of the variation in the water Fe: TP ratio. More calcium-rich lakes tended to have lower water Fe: TP ratio, suggesting that the percent marble in the catchment had some indirect influence on the Fe: TP ratio. Similarly to model 5 *a*, the CA: SA ratio was again retained and here explained an additional 14% of the variance in water Fe: TP.

In contrast, no catchment properties were found to predict the particulate or seston Fe: TP ratios. However, when considering both catchment and in-lake water chemistry variables, calcium was retained as significant independent variable (model 6).

$$(6)\ \log(\mathrm{Fe\_TP\_p}) = 1.42\ (\pm 0.33) - 0.57(\pm 0.25)\ \log(\mathrm{Cal}) \qquad r^2_{adj} = 0.12\ (p < 0.01)$$

Similarly to model 5, calcium was an independent variable retained in model 6. Here, calcium was again negatively correlated with the Fe: TP ratio in the seston (Fig. 2.1, Appendix II) and explained 12 % of the variation, which also suggests an indirect effect of the catchment bedrock composition. Figure 2.4 shows the geographical distribution of particulate Fe: TP ratio in the study lakes in relation to the underlying geology. Lakes with the lowest Fe: TP ratios include Heney, Truite, Bob, Loups and Eau Claire while those with the highest ratios include Bataille, Twin, Guilbeault, La Pêche and Gervais.

I also hypothesized that lakes more prone to iron deficiency would accumulate relatively less iron in the sediments. However, there was only a weak correlation between the water Fe: TP ratio and the surficial sediment Fe: TP ratio and no significant relationship between particulate ratios and sediment ratios of Fe: TP were found (Fig. 2.1, Appendix II). The best model predicting the sediment ratio based on basin characteristics included catcment area and housing density, but these only explained a total of 18% of the variation (mode 7 *a*).

(7 *a*) $\mathrm{Sqrt(Fe\_TP\_s)} = 1.48(\pm 0.58) + 0.35(\pm 0.13)\log(\mathrm{CA})$ $\quad r^2_{adj} = 0.09$

$+ 0.28(\pm 0.13)\,\mathrm{sqrt(HD)}$ $\quad r^2_{adj} = 0.18$

$(p < 0.05)$

Although not significantly correlated to the sediment Fe: TP ratio alone (Fig. 2.1, Appendix II), catchment area was retained as a significant variable and explained 9% of the variation, larger catchments yielding higher Fe: TP ratios in the sediments in the study lakes. House density explained an additionnal 9%. In contrast, when considering basin characteristics and water chemistry, the retained model included only loss on ignition (organic content), and surface water pH, which together explained 32 % of the variation in sediment Fe: TP.

(7 *b*) $\mathrm{Sqrt(Fe\_TP\_s)} = 6.87(\pm 1.09) - 0.03(\pm 0.01)\,\mathrm{LOI}$ $\quad r^2_{adj} = 0.32$

$- 0.04(\pm 0.02)\,\mathrm{pH}^2$ $\quad r^2_{adj} = 0.42$

$(p < 0.001)$

The organic content of surficial sediments alone explained 34 % of the variance in the sediment Fe: TP ratio. More organic-rich surficial sediments tended to have less Fe in proportion to P, which is confirmed by the significant negative correlation between these two variables (Fig. 2.1; Appendix II). Although negatively, but not significantly correlated with the Fe: TP ratio alone (Fig. 2.1; Appendix II), the surface water pH was significant when the effect of LOI was controlled for in the multiple linear regression and contributed to an additional 10% of the model prediction. Alkaline lakes exhibited lower surficial sediment Fe: TP.

Predicting algal biomass

Chlorophyll *a* is commonly used as a measure of phytoplankton biomass (Kalff, 2002). The stepwise multiple regression analysis for the prediction of this pigment based on basin characteristics retained the same parameters as that of the TP model (model 3) above: maximum depth and house density. Deeper lakes had less algal biomass while lakes with a higher house density along the shore exhibited higher algal biomass. However, less of the chlorophyll *a* variation was explained by these two variables ($r^2 = 0.17$) than by TP ($r^2 = 0.25$).

$$(8\ a)\ \text{Log(Chl)} = -0.39(\pm 0.16) - 0.09\ (\pm 0.04)\ \text{sqrt(MD)} \qquad r^2_{adj} = 0.08$$
$$+ 0.11\ (\pm 0.05)\ \text{sqrt(HD)} \qquad r^2_{adj} = 0.17$$
$$(p < 0.05)$$

As typically found for lakes worldwide (Kalff, 2002) there was a significant correlation between TP and the biomass of planktonic algae (estimated from chlorophyll *a*) in the lakes (Fig. 2.2 B) suggesting that phosphorus is the main element limiting lake productivity in these lakes. However, TKN (which essentially equates to TN in this data set given that nitrate was typically at or close to detection) was actually a better predictor of chl *a* than TP when all variables were considered in a stepwise regression analysis. TKN explained 48% of the variation in the chl *a* content in the set of lakes, while conductivity explained an additional 7% (model 8 *b*). As opposed to model 8 *a*, maximum depth did not contribute significantly when considering all other variables in model 8 *b*. The model using TP instead of TKN for predicting chl *a* concentrations showed that TP explained a slightly smaller proportion than TKN (44% vs 48%). Also, no other variables were significant in model 8 *c*.

$$(8\ b)\ \text{Log(Chl)} = -3.93(\pm 0.87) - 2.11\ (\pm 0.34)\ \log(\text{TKN}) \qquad r^2_{adj} = 0.48$$

$$- 0.51\ (\pm 0.21)\ \log(\text{Cond}) \qquad r^2_{adj} = 0.55$$

$$(p < 0.001)$$

$$(8\ c)\ \text{Log(Chl)} = -0.42(\pm 0.15) - 0.89\ (\pm 0.18)\ \log(\text{TP}) \qquad r^2_{adj} = 0.44$$

$$(p < 0.001)$$

Catchment and geochemical differences among lake hydrologic categories

Not surprisingly, the CA: SA ratio was significantly higher in drainage lakes than in isolated lakes (Fig. 2.3). The calcium concentrations were significantly higher in isolated lakes, which were also more alkaline than drainage lakes. In terms of nutrient conditions, no significant differences were detected for TP and TKN between the two lake categories. Chlorophyll *a* concentrations were also similar. Interestingly, the dissolved iron was significantly higher in drainage lakes than isolated lakes. However, the Fe: TP ratio in lake water was not significantly different in the two lake classes. In the surficial sediments though, drainage lakes had significantly higher Fe: TP ratios.

2.4. Discussion

Canada has over a million lakes and the vast majority have never been sampled. Even in the more densely populated areas of southern Canada, many lake regions are poorly studied even though development pressures are increasing. Because there are over 15,000 lakes in the Outaouais region of Québec, the tools of landscape limnology may provide a more rapid and effective approach to developing models for lake management. In this study I hypothesized that certain catchment proprieties, mainly the presence of marble bedrock, as well as the presence of other lakes in a specific lake's watershed (drainage lake vs. isolated lake), affect the relative concentrations of iron in lakes. Lakes with low iron may be more sensitive to cultural eutrophication because of the importance of iron in phosphate sequestration in lakes.

Some of the chemical characteristics of the study lakes were similar to those reported for other Shield lakes (Table 2.3). Prairie (2005) reported similar calcium concentrations and Fe: TP ratio in surface sediments for a set of four lakes in the Outaouais region with two lakes common to the current study (Heney and Bernard). D'Arcy & Carignan (1997) reported similar chlorophyll *a* concentrations in a study of 30 Canadian Shield lakes throughout the province of Québec, but higher TP than the current study. The lakes of this study also had smaller catchment areas, smaller catchment area: lake surface area ratio, lower pH, and similar Secchi depth. The lakes in the current study therefore included more headwater lakes, and these appeared relatively more oligotrophic and alkaline than the majority of Shield lakes reported in the literature.

Percent marble in lake catchment, calcium and water chemistry

The best predictive model based on basin features for Ca concentrations included the percent marble in the catchment (model 1). As a carbonate rock, marble is mainly composed of the minerals calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), both Ca-rich. The main source of Ca for a lake is its catchment bedrock and soils (Driscoll et al., 1989), so a catchment composed of Ca-rich bedrock such as marble typically yields higher in-lake Ca concentrations than more Ca-poor bedrock such as gneiss and granite, as found on the majority of the Shield. These results differ from those of D'Arcy and Carignan (1997), who found that elevation explained 32% of the variation in Ca concentration in 30 Shield lakes of Québec. Elevation is related to the hydrology of lakes as lakes higher in elevation are typically isolated lakes while drainage lakes tend to have a lower elevation. In our data set, elevation did not improve significantly the model fit. This is probably because the elevation of our study lakes covered a much smaller range (124 to 237 m.a.s.l.; standard deviation: 29.81; Table 2.1) than D'Arcy and Carignan (1997) (225 to 898 m.a.s.l.; standard deviation: 225), which may not have been sufficient to capture the potential effect of this variable on Ca.

Predicting Ca from basin features explained 12% of the variance in calcium concentrations (model 1), so there are likely other important variables that our study did not account for. D'Arcy and Carignan (1997) were able to explain 53% of the variance in lake Ca concentrations using elevation, a catchment slope index (developed by Rasmussen et al., 1989), and catchment area. The variable catchment area was considered in our study, but was not retained, as it provided no improvement to the model fit. However, our study did not include a catchment slope index, which could have increased the proportion of the variance explained by geomorphological characteristics. D'Arcy and Carignan found that catchment slope and Ca concentrations were negatively correlated. Drainage basins with steep slopes typically have thinner organic horizons and less of their surface area is covered by other wetlands (Rasmussen et al., 1989). In contrast, low slopes can increase the residence time of surface runoff and groundwater, which allows more time for water to reach chemical equilibrium with the bedrock it is in contact with (D'Arcy & Carignan, 1997).

In eastern North America, the last glaciation (Wisconsinan, ca. 80 to 12 thousand years BP) left a large number of lakes, many of which are drainage lakes, i.e. stream-fed and lake fed. In the current study, the majority of lakes belonged to this category and had a relatively large CA: SA ratio. In contrast, six lakes were isolated lakes, with no other major water bodies in their catchment: Demi-Lune, Fraser, Gervais, Kalalla, Truite, Vert. These two hydrological connectivity categories showed some significant differences in their chemistry. The calcium concentrations in isolated lakes were significantly higher than in drainage lakes (Fig. 2.3). This may be due to the bedrock composition of the catchment. Even though isolated lakes have much smaller catchment areas, the percent marble in their catchment was higher in this data set (although not significant using a p-value threshold of 0.05; Fig. 2.3), which likely exported large amounts of Ca in these lakes. Importantly, sample size is different between the two lake categories (n= 25 for drainage lakes and n= 6 for isolated lakes). This difference is nonetheless representative of the region as a majority of lakes on the Canadian Shield are drainage lakes. Furthermore, the type of land use, which was not analysed in this study, may explain the differences in Ca concentrations between drainage and isolated lakes. As forests on the Shield are prone to Ca deficiency particularly given the history of acid rain in Canada, Ca may be more retained in forested areas and therefore less exported to lakes. Further land use analyses of each lake's catchment would be necessary to evaluate whether Ca concentrations in drainage lakes vs. isolated lakes influenced by land clearing.

Even though calcium concentrations were lower in drainage lakes, none of the lakes exhibited Ca concentrations that might lead to deficiency. Laboratory analyses have found that Ca concentrations < 1.5 mg/L affect the growth, reproduction and survival of common crustaceans of the genus *Daphnia* (Ashforth & Yan, 2008). The lowest Ca concentration in our study lakes was

4.32 mg/L in Lake Victoria (Appendix I). Therefore, Outaouais lakes do not seem to suffer the severe Ca depletion observed elsewhere on the Canadian Shield, in the Experimental Lake Area for example (Jeziorski et al., 2014). Over the last three decades, eastern North America has been subject to major Ca losses due to depletion of the base cation reservoirs in catchment soils at a faster rate than replenishment through geochemical weathering of the underlying bedrock (Kirchner & Lydersen, 1995; Houle et al., 2006). The soil Ca depletion is caused by the biomass removal through repeated timber harvest (e.g Likens et al., 1996; Federer et al., 1989; Bailey et al., 1996), as well as the mobilization of base cations due to acid deposition (Likens et al., 1996). This situation has brought growing concern that soil Ca losses may lead to reduced tree growth, increased forest dieback, decreased freeze tolerance, and increased susceptibility to drought and diseases (DeHayes et al., 1999). In freshwater ecosystems, Ca declines may have serious ecological consequences should concentrations fall below the critical threshold of Ca-demanding organisms such as cladoceran zooplankton (e.g. daphniids) (Jeziorski et al., 2014). These small invertebrates are considered a keystone species (e.g. Smol, 2010) as they often are the dominant algal grazers and are important prey items for fish and invertebrate predators (Wissel et al., 2003). Because of their intermediate trophic position, changes within their communities may have considerable impacts on lake ecology (Jeziorski et al., 2014).

Other than the calcium concentrations, the percent marble in the catchment had a significant effect on several geochemical characteristics of lake water. Lakes with a higher proportion of marble in their drainage basin generally had a higher pH (model 2), as well as higher alkalinity (model 8, Appendix III). Alkalinity is a measure of the acid neutralizing capacity, determined by the total hydroxyls (OH), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions (Kalff, 2002). The contact of runoff water with the marble bedrock allows carbonate ions contained in marble to dissolve, then get carried to a lake system where they contribute to the alkalinity of the receiving lake. Similarly, isolated lakes had higher pH than drainage lakes (Fig. 2.3). As mentioned earlier, isolated lakes tended to have a higher proportion of marble in their catchment, and the carbonate ions contained in marble contribute to alkalinity.

Nutrients, productivity and human disturbance

Even though TP is typically the macronutrient limiting the phytoplankton productivity in lakes (Schindler, 1974) and that in all of our study lakes, the TN: TP ratio is above 17, which indicates P limitation (Hellström, 1996), our linear models suggest that TKN ($r^2_{adj} = 0.48$, model 8*b*) exhibited a similar predictibility with algal biomass to TP ($r^2_{adj} = 0.44$, model 8*c*, Appendix III). These results differ from those reported in the literature. For example, D'Arcy & Carignan (1997) found that TP was the most important predictor of chlorophyll *a* and explained 52% of the variation in a set of 30 Shield lakes of southeastern Québec. However, the only form of nitrogen the authors measured was NO_3^- (nitrate), which was not significantly correlated to chlorophyll *a*. In our set of lakes, drainage lakes vs. isolated lakes showed no significant differences in TP, TKN and chlorophyll *a* concentrations so it appears that hydrological connectivity does not have major impacts on the in-lake nutrient concentrations and phytoplankton abundance. Similarly, Soranno et al. (2015) did not capture different nutrient concentrations in the 346 north temperate lakes of their comparison of lakes with different hydrological connectivity.

Among the basin characteristics, only maximum depth had a significant impact on the chlorophyll *a* concentrations. Maximum depth explained 8% of the chlorophyll *a* variation and had a negative slope (model 8 *a*), and the Pearson correlation coefficient was also negative (Fig. 2.1). Moreover, this variable explained 31% of the variation in TKN (model 11 *a*, Appendix III) and 11% of the variation in TP. These results are supported by other studies such as Duarte and Kalff (1989) who found that lake mean depth was among the variables that best described chlorophyll *a* concentrations in over 200 temperate lakes of North America. With increasing depth, lakes tend to lose a greater proportion of nutrients through the process of sedimentation (Cardoso et al., 2007). Shallow lakes typically do not stratify, which allows nutrients to remain in circulation and accessible for phytoplankton growth. In this sense, lake depth is a key factor that influences the relationship between lake water nutrient content and morphology (Huo et al., 2015).

Human disturbance, as measured by the house density on the lakes' shoreline, had some impact on the lake nutrients and productivity. The house density was the second variable retained in the model predicting chlorophyll *a* based on basin characteristics (model 8 *a*). Similarly, house density was the second variable predicting TP in the model based on basin characteristics (model 3) and in the model based on all variables (model 3 *a*, Appendix III). The presence of houses along a lake's shoreline typically increases the nutrient import through several processes. For instance, house development implies tree cutting, landscape modification, application of P-rich fertilizers to lawns, possible leaks from septic tanks, as well as compaction of soil and increases in impervious surfaces which increases runoff.

Different tools have been created to model the effects of human activities on aquatic systems and assist lake managers in lakeshore development decision-making processes. Notably, the Ministry of Environment has used the Lakeshore Capacity Model (LCM), developed by Dillon and Rigler (1975), which predicts the impact of lakeshore development through the entire catchment of a lake, including downstream lakes (Hutchison et al., 1991). The model predicts TP concentrations and several trophic status indicators, using empirical relationships that relate natural and anthropogenic P sources, as well as hydrologic and morphometric data, in order to establish a specific lake's P budget, and therefore determine the maximum number of dwellings that can be built on a lake's shoreline without inducing significant changes in the nutrient levels (Hutchison et al., 1991). Importantly though, there can be a significant lag period between the P addition and its movement to the lake depending on factors such as the distance between the septic system and the lake, the bedrock composition, the vegetation cover and the soil P binding capacity. This validates the need to use both in-lake measurements and modeled P concentrations. Our findings support that an increasing number of houses along the lakes' shoreline has measurable impacts on the lakes' nutrient conditions and algal biomass. Tools like the LCM could help lake managers in the province of Québec to set maximum lakeshore development in order to prevent eutrophication problems.

Lake catchment properties and iron-phosphorus dynamics

Drainage lakes had significantly higher sediment Fe: TP in surficial sediments (Fig. 2.3). The Precambrian Shield landscape is a mosaic of interacting landforms including wetlands, peatlands, running waters and lakes. Each landform has unique characteristics that influence the flux of chemical and nutrients to downstream lakes and streams (Allan et al., 1993). Typically, wetlands are an important Fe source to downstream lakes (Passy, 2010) while lakes often retain Fe (Carignan, 2003). As drainage lakes comprise both wetlands and headwater lakes in their catchment, their sediment Fe: TP may reflect an interplay of different landforms that export (wetlands) and retain (headwater lakes) iron in their catchment. Isolated lakes have much less wetlands and no headwater lakes in their catchment; therefore their sediment Fe: TP ratio is likely more a function of the bedrock geology, atmospheric deposition and in-lake conditions rather than upstream water bodies.

Even though the difference in the surface water Fe: TP ratio was not significant between drainage and isolated lakes, there was some evidence that catchment physical properties affect the Fe: TP dynamics. In the stepwise regression analysis considering only basin characteristics, the only variable retained to predict water Fe: TP was the CA: SA ratio (model 5 *a*), which explained 14% of the variation in Fe: TP. In our study lakes, larger CA: SA ratios (drainage lakes) had more iron in relation to TP. When considering all variables (model 5 *b*), the CA: SA ratio was again retained, but as the second variable and explained an additional 14% of the variation in Fe: TP. Again, lakes with a higher CA: SA ratio are likely to have more wetlands in their catchment than lakes with a low CA: SA ratio. Wetlands are important sources of Fe and can export important quantities of this element to downstream lakes (Passy, 2010). Additionally, large catchments allow more time and space for surface water and groundwater to capture elements such as iron and reach chemical equilibrium with the bedrock it is in contact with. Because a vast majority of the land cover in our study area consists of forests, the inflowing water likely does not capture much P in comparison to cations from the bedrock interaction. However, the specific area of wetlands vs. forests was not calculated in the present study, further analyses would be required to draw specific conclusions regarding the effect of this land cover on the in-lake water chemistry.

Correlations between dissolved iron and alkalinity ($r = -0.36$, $p = 0.048$), as well as iron and pH ($r = -0.49$, $p = 0.005$) were negative and significant (Appendix II). Molot & Dillon (2003) found similar correlations between these variables in a set of seven oligo- to mesotrophic study lakes in the Dorset study area in central Ontario, also located on the Precambrian Shield. The ferrous iron concentrations typically increase as pH decreases (<6) because acidity inhibits the oxidation of ferrous iron to ferric iron by oxygen (Shaw, 1994). These correlations are consistent with the hydrological categories as the more alkaline (isolated) lakes showed lower dissolved iron concentrations than more acidic (drainage) lakes (Fig. 2.3). Drainage lakes in the current study had significantly lower pH and their acidity likely inhibited the oxidation of ferrous to ferric iron.

The presence of marble in the catchment appeared to have some, although sometimes indirect, influence on the in-lake Fe: TP dynamics. Calcium concentration was the first variable retained in the stepwise linear regression, and explained 17% of the variation in surface water Fe: TP ratios, with a negative slope (model 5 *b*). Similarly, 12 % of the variation in the seston Fe: TP was explained by calcium concentration (model 6). As percent marble in the catchment and calcium concentrations were positively and significantly correlated (Appendix II), this suggests that lakes with more marble in their catchments tend to have lower Fe: TP ratios. This provides some evidence that lakes with marble in their catchment might be more vulnerable to iron deficiency. To our knowledge, only one previous study suggested lake iron deficiency caused by the large extent of marble bedrock in a lake's catchment (Carignan, 2003). This unpublished study also suggested that the presence of many headwater lakes in the study lake's catchment acted as a Fe trap, reinforcing the iron deficiency.

Internal loading of P and Fe in productive lakes can have important consequences for the phytoplankton composition and abundance and can lead to cyanobacteria dominance, which may produce toxins affecting humans and wildlife, and deep water anoxia leading to fish kills (Havens, 2008). Cyanobacteria have higher iron requirements than their eukaryotic competitors and the N-fixation process further increases their Fe needs (Murphy et al, 1976). Cyanobacteria can acquire iron through direct transportation of Fe^{2+} through their cell membrane, but if ferrous iron is scarce, they secrete siderophores in order to meet their high Fe requirements (Brown & Trick, 1992). These low molecular weight organic chelators have a high affinity for Fe^{3+}, they can bind free Fe^{3+} as well as cleave Fe^{3+} bound to dissolved organic matter complexes (Neilands, 1995). Ferric iron is then delivered to the cell membrane, thus creating a Fe pool only accessible to cyanobacteria; Fe^{3+} is then reduced and transported into the cell as ferrous iron (Molot et al., 2014). This strategy allows cyanobacteria to lock ferric iron into siderophore-bound complexes that are unavailable to their eukaryotic competitors that do not have a siderophore-Fe uptake system (Molot et al., 2014).

Even though the current study revealed some evidence that lakes with a high proportion of marble in their catchment are likely more vulnerable to iron deficiency, we obtained no evidence that Fe-deficient lakes were more vulnerable to eutrophication. Indeed, neither the water, seston nor sediment Fe: TP ratios were retained as significant variables in predicting in-lake TP, TKN, nor chlorophyll *a* concentrations. Nonetheless, lakes with low Fe: TP ratios in the sediments, and those where anoxic conditions develop over the growing season, are typically more susceptible to experience internal loading, which leads to increases in the water column TP concentrations. In a set of fifteen Danish lakes, Jensen et al. (1992) found that lakes with a Fe: TP ratio >15 (by weight) in surficial sediments were able to retain P for as long as oxic conditions were maintained. In our set of lakes, only Lakes Bernard, Jean Venne, Bitobi, Perdrix and des Loups had surficial sediment Fe: TP above the threshold suggested by Jensen et al., 1992 (Appendix I), suggesting all the other study lakes are vulnerable to internal loading if the hypolimnetic oxygen concentrations get sufficiently low. In fact, internal loading has already been observed in Heney Lake, even in the presence of oxygen. Carignan (2003) measured that a total of ~200 kg/year in the winter and ~1000 kg/year of P in the summer were liberated from the sediments over the years 2002-2003.

Important changes to lake processes are expected with the current climate change, including the extension of the growth season, higher surface water temperature (Kling et al., 2003; McFadden et al., 2004) leading to changes in the timing, duration and strength of thermal stratification (Tadonleke et al., 2009). These changes will likely stimulate algal productivity and may lead to hypolimnion oxygen depletions, even in oligotrophic lakes where bottom water anoxia typically does not arise (Leblanc et al., 2008). As a result, lakes with low Fe: TP, like the majority of our study lakes, are likely to experience internal loading, especially at the end of the growth season when the hypolimnion oxygen concentration is at its lowest. This could have important implications for lake ecology such as increases in the water column P concentrations, which would further increase the lake's productivity. Also, cyanobacteria may have a competitive advantage in these conditions as they have the ability to migrate downwards into the hypolimnion to obtain the Fe^{2+} and orthophosphate released from the sediments in the hypolimnion, as well as create a Fe-pool unavailable to their eukaryotic competitors thanks to the siderophores they produce (Molot et al., 2014). Fall cyanobacterial blooms have already been observed in the

Ottawa-Gatineau region since 2001, including in Lac des Loups and Lac à La Pêche (Leblanc et al., 2008). Such blooms had not been reported previously in these oligo-mesotrophic lakes with TP concentrations below the threshold for the onset of cyanobacterial dominance (Pick & Lean, 1987; Downing et al., 2001) and may be linked to the interplay of Fe: TP dynamics, internal loading and climate change effects.

Table 2.1 Summary of physical and surface water chemistry characteristics of the 31 study lakes in the Outaouais, western Québec.

Variables	Variable	Mean	Minimum	Maximum	Median	Standard deviation
Elevation (masl)	Elev	173.35	124	237	171	29.81
Surface area (hectares)	SA	117.31	3.07	1231.14	31.88	252.19
Catchment area (hectares)	CA	1569.72	14.43	7867.47	473.06	2218.15
Catchment area: surface area	CA_SA	34.1	2.28	181.75	8.04	53.1
Max depth (m)	MD	17.69	1	53	15	12.72
House density (#/km shoreline)	HD	6.5	0.19	16.45	5.84	4.7
Percent marble in catchment (%)	MP	32.25	0	100	26.5	30.59
pH	pH	8.11	6.75	8.74	8.12	0.45
Conductivity (µS/cm)	Cond	140.33	43.7	242.8	131.5	56.15
TP (µg/L)	TP	6.98	2	22.5	6.5	3.81
TKN (µg/L)	TKN	324.19	190	570	310	84.89
Fe dissolved (µg/L)	Fe_d	16.48	0.7	114.25	6.85	27.56
Fe:TP water	Fe_TP_w	2.37	0.09	12.28	1.14	3.16
Calcium (mg/L)	Cal	21.24	5.7	40.8	19.4	9.15
Secchi (m)	Sec	4.35	1.2	8.6	4.18	2.13
Alkalinity (mEq/L)	Alk	78.39	15.25	170.3	74	37.56

Table 2.2 Seston and sediment chemistry of the 31 study lakes in the Outaouais, southwestern Québec.

Variable	**Variable**	**Mean**	**Minimum**	**Maximum**	**Median**	**Standard deviation**
Planktonic chlorophyll *a* (μg/L)	Chl	2.35	0.31	7.62	2.17	1.54
TP particulate (μg/L)	TP_p	4.34	1.99	15.74	3.81	2.65
Fe particulate (μg/L)	Fe_p	25.35	4.58	104.81	15.48	25.04
Fe:TP particulate	Fe_TP_p	6	1.32	15.5	5.28	3.85
TP in surface sediments (g/kg)	TP_s	20.44	0.72	5.28	1.70	0.86
Fe in surface sediments (g/kg)	Fe_s	18.99	1.59	53.10	18.03	9.57
Fe:TP in surface sediments	Fe_TP_s	10.09	1.52	20.94	9.7	4.78
Sediment loss on ignition (%)	LOI	42.98	7.75	83.6	40.11	16.49

Table 2.3 Comparison of variables with other lake surveys in North America.

Variable	Mean	Minimum	Maximum	Median	Standard deviation	Author(s)
Catchment area (hectares)	1569	14.43	7867	473	252	Current study
	264	27	713	206	192	D'Arcy & Carignan (1997)[1]
	3855.5	261	29843			Pinel-Alloul & Méthot (1990)[2]
Catchment area: surface area	34.1	2.28	181.75	8.04	53.1	Current study
	7.55	3.55	15.87	6.83	3.13	D'Arcy & Carignan (1997)
Chl a (μg/L)	2.35	0.31	7.6	2.17	1.5	Current study
	2.72	0.6	7.1	2.13	1.72	D'Arcy & Carignan (1997)
TP (μg/L)	6.98	2	22.5	6.5	3.81	Current study
	8.66	4.2	14.3	8.37	3	D'Arcy & Carignan (1997)
	11.4	2.2	59.7			Sorichetti et al. (2014)[3]
pH	8.11	6.75	8.74	8.12	0.45	Current study
	5.92	5.06	6.7	5.95	0.47	D'Arcy & Carignan (1997)
	6.0	5.2	8.3			Pinel-Alloul & Méthot (1990)
	6.0	5.6	6.6	5.8	0.42	Molot & Dillon (2003)[4]
	7.4	5.4	9.1			Sorichetti et al. (2014)
Cal (mg/L)	21.24	5.7	40.8	19.4	9.15	Current study
	22.33	13.5	28.6	22.6	5.05	Carignan (2003)[5]
Fe_d (μg/L)	16.48	0.7	114.25	6.85	27.56	Current study
	10.2	2.9	267.3			Sorichetti et al. (2014)
	2.26	0.16	10.97	0.93	3.09	North et al (2007)[6]
Fe_p (μg/L)	25.35	4.58	104.81	15.48	25.04	Current study
	34					Murphy et al. (1976)[7]
	7.44	0.42	27.73	4.01	8.64	North et al. (2007)
Fe_s (g/kg)	19	15.85	53.1	18.03	9.57	Current study
	24.76				4.43	Beutel et al. (2008)[8]
	47.5					Carignan (2003)[5]
Fe_TP_s	10.09	1.52	20.94	9.7	4.78	Current study
	11.75	5.86	19.29	10.93	5.65	Prairie (2005)[9]
	13	9	19		3	Dillon et al. (1990)[10]
Secchi (m)	4.35	1.2	8.6	4.18	2.13	Current study
	4.7	1.9	9.6	3.9	1.9	D'Arcy & Carignan (1997)
	3.7	1	8			Pinel-Alloul & Méthot (1990)

[1] Study of 30 Shield lakes in the province of Québec, north of Québec City
[2] Study of 45 Shield lakes throughout the province of Québec, including the Outaouais region
[3] Study of 25 oligo-mesotrophic lakes in the Laurentian Great Lakes - St.Lawrence River Basin, Ontario
[4] Study of 7 oligo- to mesotrophic Shield lakes of the Dorset study lakes in Central Ontario
[5] Study of 11 Shield lakes in the Outaouais region, including Heney, Vert and Noir
[6] Study of lake Erie, Ontario
[7] Study of Heart Lake, a 16 hectares lakes in the St. Lawrence lowlands, north-west of Toronto
[8] Study of Lake Matthews, a 10 km^2 oligo-mesotrophic lake in Southern California
[9] Study of 4 Shield lakes in the Outaouais, including Lake Heney and Bernard
[10] Study of Blue chalk lake, an oligotrophic Shield lake in central Ontario

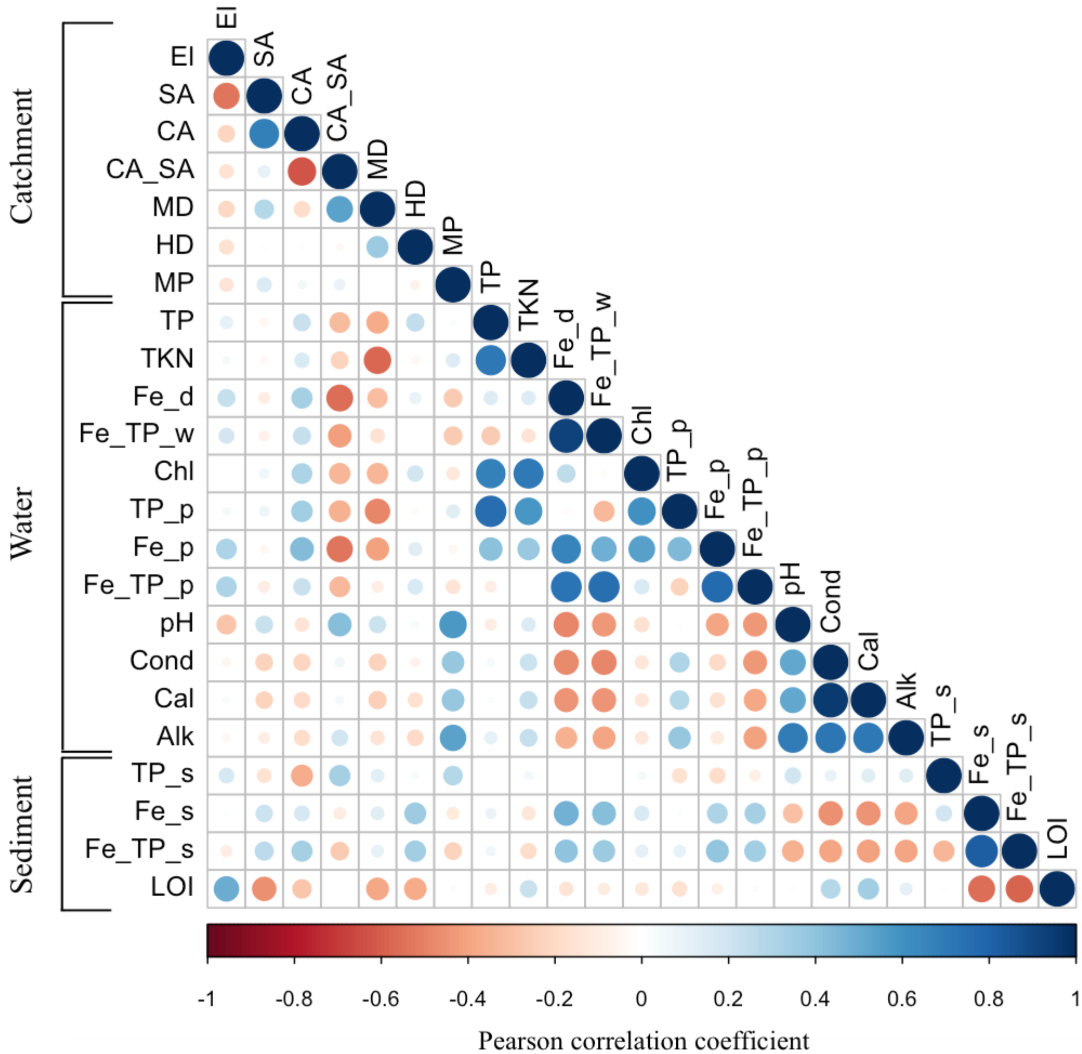

Figure 2.1 Pearson's correlation matrix of basin, water and sediment characteristics. Red indicates a negative correlation while blue indicates a positive correlation. Correlation coefficients > 0.65 are significant based on Bonferroni-adjusted probabilities. Actual correlation coefficients and the related significance level are given in Appendix II.

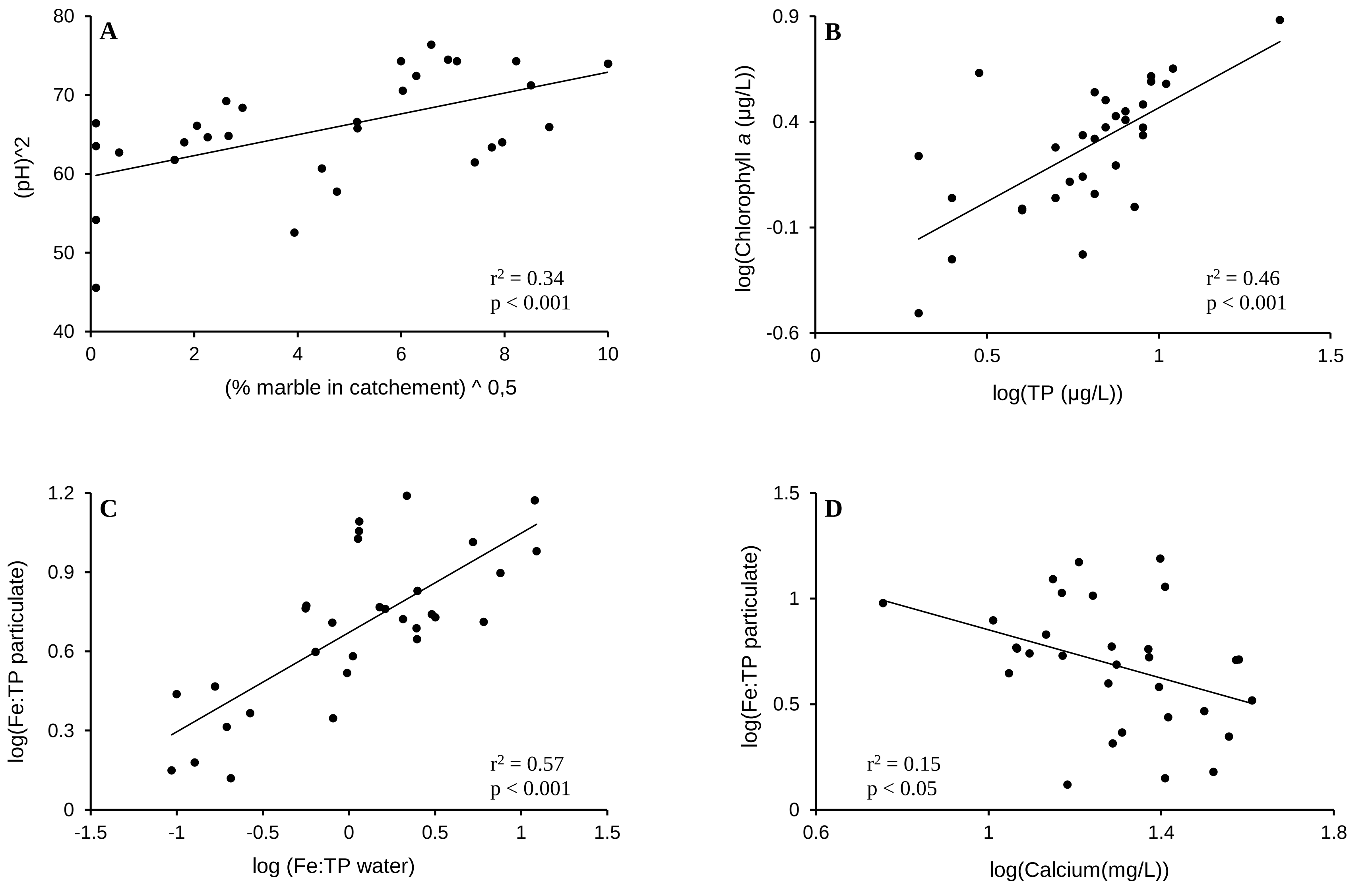

Figure 2.2 Simple linear regression models of A) pH vs. marble percent in catchment, B) chlorophyll *a* vs. TP, C) particulate Fe:TP vs. surface water Fe:TP and D) particulate Fe: TP vs. Calcium, in the 31 study lakes in the Outaouais region, southwestern Québec.

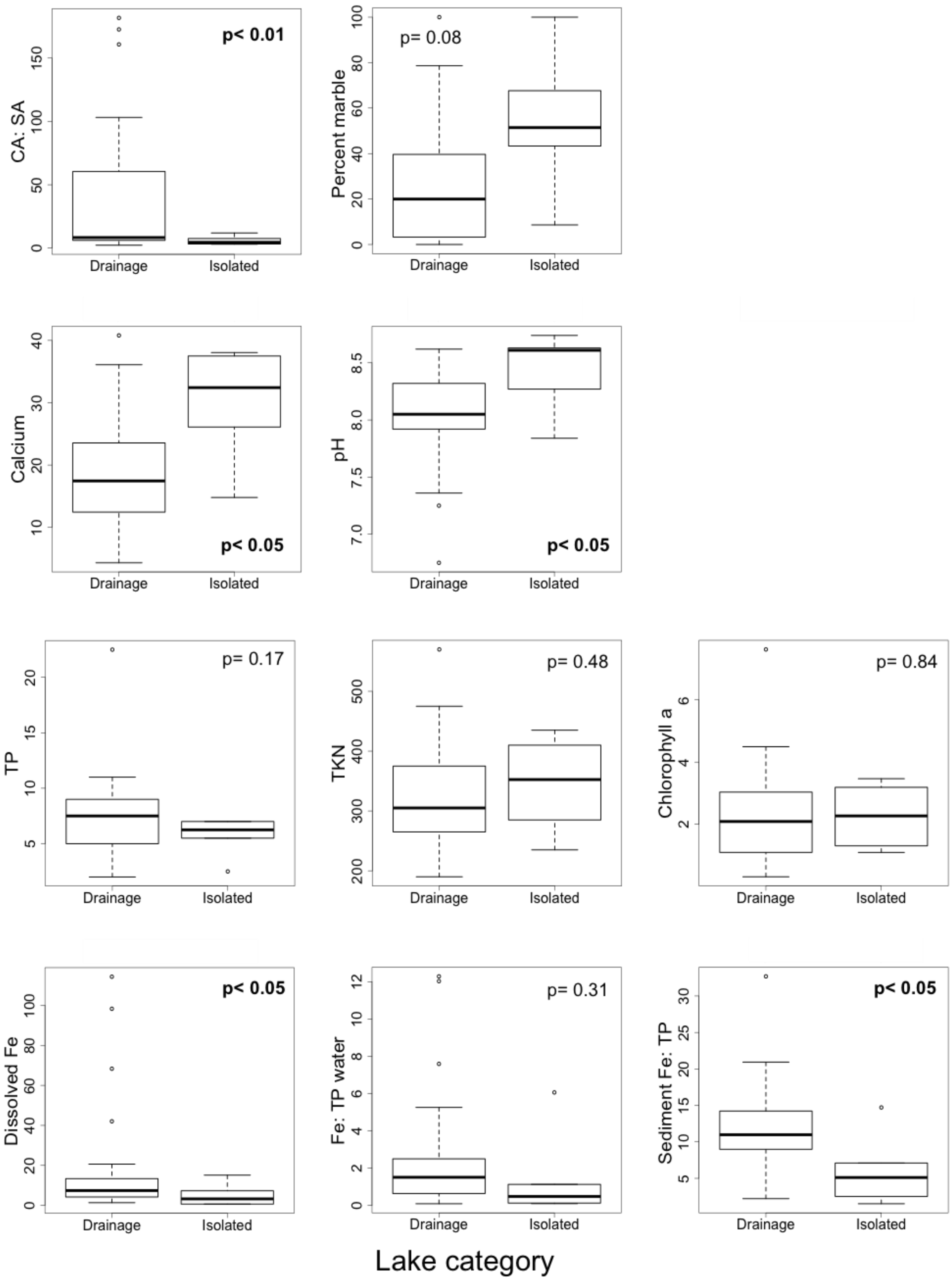

Figure 2.3 Boxplots of catchment and water chemistry characteristics by lake class. The p-values are shown for a two-way t test to test the difference among the two lake classes for each variable, p-values in bold are significant at $p \leq 0.05$. N= 6 for isolated lakes and N=25 for drainage lakes.

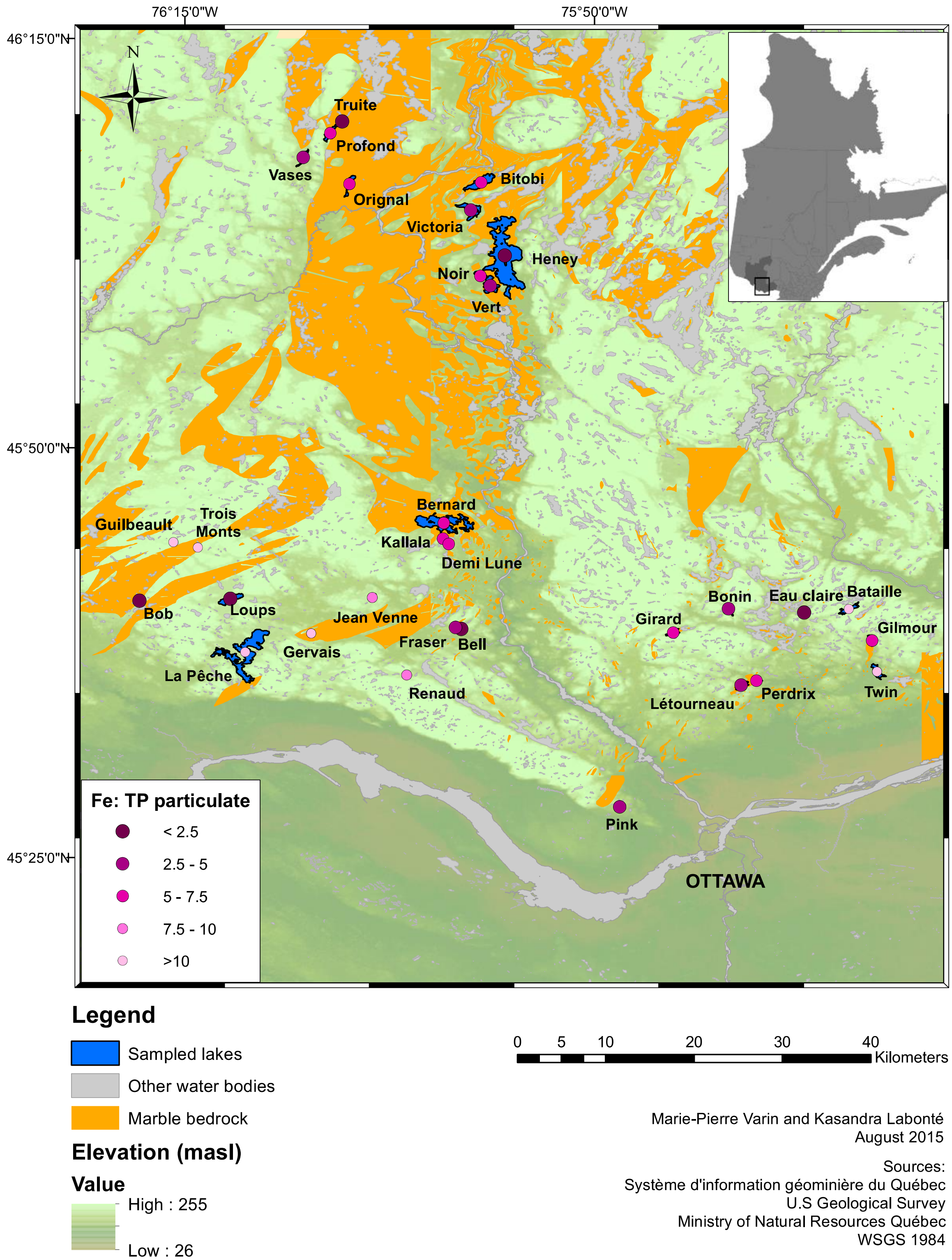

Figure 2.4 Fe: TP ratio in the seston in the 31 study lakes in the Outaouais region, southwestern Québec

3. Paleoecological reconstruction of Heney Lake's recent history

3.1. Introduction

Human-induced eutrophication, the nutrient enrichment of aquatic systems leading to an increase in productivity, is considered the primary problem currently facing most surface waters (Smith & Schindler, 2009; Carpenter et al., 2011). The main nutrient responsible for eutrophication of freshwater ecosystems is phosphorus (P) (Schindler, 1974) as it typically is the principal nutrient limiting algal growth (Kalff, 2002), but nitrogen may also play a role in some lakes (e.g. Smith et al., 1999; Winter et al., 2002). Iron can also play an indirect role in nutrient dynamics; the oxidized form of iron (Fe^{3+}) binds to P and the complex formed (FeOOH~P) is insoluble and sinks to the sediment surface where it remains if oxic conditions are maintained (Mortimer, 1942). Consequences of eutrophication include excessive increase in plant productivity, blooms of harmful algae, increases in the frequency of anoxic events, and fish kills (Carpenter, 2005). From a human perspective, eutrophication can impair water quality and increase costs for water purification, as well as decrease the recreational and aesthetic value of water bodies.

In order to address adequately eutrophication problems, a holistic approach that encompasses both terrestrial and aquatic systems is necessary. The effective management of lakes requires an in-depth understanding of in-lake processes as well as the causes and impacts of environmental stressors that may come from the surrounding catchment. Moreover, the pre-disturbance nutrient conditions need to be understood if managers wish to set realistic goals for a specific water body, as conditions vary from one lake to the other depending on climate, local geology, morphometry and catchment proprieties for example. In North America, freshwater ecosystems have been subject to anthropogenic pressures for ~150 years (e.g. Vermaire et al., 2012) but for a vast majority of these, long-term monitoring of limnological conditions is non-existent. Other tools are therefore needed to establish pre-disturbance conditions and therefore assist in the lake management decisions. One common and effective method is the use of paleolimnological techniques, using the material accumulated in lake sediments, which act as an archive of past limnological conditions (e.g. Smol, 2008, 2010; Ginn et al., 2015). The sediment material can then be used to reconstruct changes in the lake and its catchment (Smol, 2008).

In a majority of fresh water lakes, diatoms (Bacillariophyceae) often represent the dominant primary producers, frequently contributing to more than half of the primary production (Smol, 2008; Rühland et al., 2015). These unicellular microscopic algae (typically 5-200 μm) are a preferred high-quality food source for primary producers and are an essential link for the energy transfer to higher trophic levels of the food chain (Smetacet, 1999; Reynolds, 2006) and for nutrient cycling (Tréguer, 2002). Diatoms have a high taxonomic diversity and are abundant in a wide array of aquatic systems (Julius & Theriot, 2010); they are particularly sensitive to changes in the physical and chemical conditions (Rühland et al., 2015), namely pH, nutrient concentrations and organic matter content (e.g. Smol, 2008; Tremblay et al., 2014). Diatoms leave fossil remains as they produce a siliceous cell wall (frustule) composed of two interlocked theca, or valves (Smol, 2008). These frustules are resistant to physical breakage, bacterial decomposition and chemical dissolution and are thus well preserved in sediments (e.g. Smol, 2008). Diatoms are therefore particularly suitable for paleolimnological reconstruction, as 1) they are sensitive to changes in environmental conditions and 2) their cell walls are well preserved in sediments and allow relatively easy identification (e.g. Cohen, 2003; Smol et al., 2005; Tremblay et al., 2014). By determining the species-environment relationships and the ecological preferences of different diatom taxa, one can develop inference models that allow for the reconstruction of environmental variables. The usefulness of a model is typically restricted to its region of origin (Smol, 2008). By using a regional training set, one also captures most of the environmental and biotic variation, including regional climate effects and water chemistry, which can affect the diatom community. Additionally, the morphological variations in the species found in a sediment core are likely more similar to those in nearby lakes and will allow a better association of downcore fossil species with surficial sediments species of the training set lakes. Each reconstruction therefore involves the sampling of lakes near the lake of interest in order to establish the regional species-environment relationships and the preferred conditions of each diatom taxa.

Diatoms have been linked to lake-specific changes in a multitude of studies (Smol, 2008), but also to broader climate-related variables in more recent studies (Rühland et al., 2008). Indeed, climate change is increasingly acknowledged as an important driver of canges in lake ecosystems (George & Harris, 1985; IPCC, 2001; Williamson et al, 2009; Berthon et al., 2014). Many studies worldwide have shown links between variations in the climate and ecological processes and the response in diatom community dynamics and species assemblage (Catalan et al., 2002; Smol et al., 2005; Pannard et al., 2008; Winder & Hunter, 2008; Smol & Stoermer, 2010). The phytoplankton dynamics and community structure are widely affected by climate-related physical proprieties in lakes including the length of the open-water season, the timing, duration and strength of the stratification period, the timing and strength of the spring freshet, and the duration of spring overturn (Rühland et al., 2008). The effects of climate change on lakes vary with latitude and other geographic factors with northern latitudes experiencing the greatest rates of change (IPCC, 2013).

The landscape of the Outaouais, a temperate region in southwestern Québec, is dominated by water with over 15,000 lakes (Government of Québec, 2002). A vast majority of the Outaouais is located on the Canadian Shield, mostly composed of granite and gneiss, with some calcitic and dolomitic marble (Rock Ontario, 1994; Carignan, 2003). The development of the region began in the early XIXth century (NCC, 2005). The logging industry rapidly became important and with an increasing demand for wood from the United States and abroad, starting in the middle of the XIXth century, the entire Gatineau River Valley was quickly exploited (Messier, 2007). Today, the main economic activity in the Outaouais remains the logging industry, with some pasture and forage crop. The region also has many cottages and houses along its numerous lakes and rivers. Nonetheless, a large portion of the territory remains forested.

Despite the proximity of Outaouais lakes to a major urban area, the national capital of Canada, their limnological conditions have not been well characterized. Some limnological and paleolimnological studies have been conducted in the southwestern Outaouais, but these focused more on forest composition changes, fire occurrences, precipitation history, changes in fossil cladoceran communities and temperature reconstruction and that, on a longer time scale than the current study (Paquette & Gajewski, 2013; Lafontaine-Boyer & Gajewski, 2014; Cooper, 2015). To our knowledge, there are no published diatom training sets specific to the Outaouais region. Even though the water quality is generally good in this region (Santé Publique Québec, 2008), many lakes are exposed to direct and indirect anthropogenic pressures such as nutrient addition through forest clearing, agriculture and fish farming, introduction of non-native species, hydroelectric dams, housing development and, to a broader sense, climate change. Many citizen-based lake associations are making efforts to preserve aquatic ecosystems and reduce the nutrient concentrations to prevent further eutrophication. However, a majority of these lakes have only been monitored recently, if at all, and so there is a need to establish the paleolimnological conditions of these lakes in order to set lake-specific goals that are realistic.

The objective of this study was to reconstruct the history of one of the Outaouais lakes, Heney Lake, which has been subject to cultural eutrophication, in order to establish a realistic nutrient mitigation goal. During the 1990s, a trout fish farm was operated in a bay of Heney Lake, which was blamed for causing eutrophication problems. As the lake was deemed iron deficient, a treatment was performed in 2007, during which a large amount of iron chloride was spread at the lake's surface to reduce the phosphorus concentration. However, the pre-disturbance nutrient concentrations are not known and so the target might be unrealistic or not sufficiently ambitious for this specific lake. Determining the pre-European settlement trophic conditions is important in the current context as authorities wish to restore the lake. In order to achieve this goal, I chose to build a reconstruction of TP based on diatoms as they are sensitive indicators of historic changes in the water conditions and are well preserved in sediments (e.g. Smol, 2008).

3.2. Material and methods

Study site: Heney Lake

Heney Lake (45.6715ºN, 75.5683ºW) is a dimictic lake located on the Canadian Shield, in southwestern Québec. Unlike the majority of lakes of the Precambrian Shield, Lake Heney and half of its watershed lies on calcitic and dolomitic marble (Appendix IV), which have a low concentration of certain minerals such as iron, aluminum and sulphur (Carignan, 2003). The bedrock is locally overlaid by thin glacial deposits of the Wisconsinan glaciation, 80 to 12 thousand years BP (Richmond & Fullerton, 1986). This particular bedrock composition yields a water chemistry characterized by relatively high calcium and magnesium concentrations (10-30 mg/L and 1-3 mg/L, respectively), as well as a slightly alkaline pH (7-9) (Chapter 2).

Lake Heney's watershed is 78.6 km^2, of which 95% is covered with 40-100 years old mixed deciduous forest (Carignan, 2005). The rest of the catchment consists of deforested land, mainly dedicated to forage crop and pasture (Carignan, 2003; chapter 2). The lake's shape is elongated in a north-south axis and covers over 12 km^2, with 32.6 km of shoreline. The maximum depth is 34 m and its volume is ~17.23 x 10^6 m^3. The water residence time is 6-7 years (Prairie, 2005).

The economic development of the Southern Outaouais region was mostly based on the logging industry, with some agriculture and rural tourism, starting in 1800 with the arrival of the American Loyalist Philemon Wright (Tourisme Outaouais, 2014). The logging industry, and some farming activity, began in ~1850 in the vicinity of Heney Lake. The first cottage along the shore of Heney Lake was built in 1902 and the first commercial fishing club, *Northfield Lodge Club*, opened in 1925 (Messier, 2007). The development continued in the 1920s and subsequently. Notably, a fish farm (Truiticulture S.L.) raised trout in Whitefish Bay (North-East portion of Lake Heney) from 1994 to 1999. Today, about 350 cottages and houses exist along the shores of Lake Heney, with five fishing and hunting outfitters as well as a sawmill (FONDEX Outaouais, 2005).

Heney Lake is currently mesotrophic and epilimnetic summer TP concentrations have been varying between 10 and 20 µg/L since 2007 (Carignan, 2012; Chapter 2). From July to October, TP increases significantly at depths below 20 m, and the hypolimnion normally undergoes anoxia at the end of the summer, and gets re-oxygenated during the fall overturn (Carignan, 2012). The DO at 25 m deep was 2.36 mg/L when sampled in September 2013, and 0.85 mg/L in the following month The TKN concentrations were 310 µg/L and 265 µg/L when sampled in September 2013 and March 2014, respectively. The depth of the thermocline in September 2013 was ~11.5 m. The epilimnion is slightly alkaline with a pH of ~8.7, while the hypolimnion is circumneutral. The calcium concentration in surface waters was 19.4 mg/L when sampled in September 2013 and dissolved Fe concentration was 20.5 µg/L. The Secchi depth was ~5.35 m and so the photic zone was ~10.7 m deep (Wetzel, 2001).

Unlike a majority of lakes, internal loading of P is observed under oxic conditions in lake Heney (Carignan, 2003) and during periods of anoxia in the hypolimnion, P release is not concomitant to a Fe^{2+} release (Carignan, 2003). In a study of the P dynamics in lake Heney and 10 other lakes in the vicinity, Carignan (2003) found no significant correlation between in-lake TP and the watershed to lake area ratio, the importance of habitations, wetlands or agricultural lands in the watershed, unlike in a majority of lakes in other regions of the Canadian Shield. This suggests that these P inputs are minor compared to the internal dynamics.

The oxic P release and the low P-binding capacity of sediments in Heney Lake strongly suggest iron deficiency (Carignan, 2003). This deficiency is likely due to natural causes as Heney Lake receives small amounts of iron from its catchment due to its bedrock composition (marble) and the seven headwater lakes in its catchment may trap the little iron exported from the watershed. However, this condition was probably aggravated by the human activities in the lake and its watershed, namely the logging industry and the building of houses, lodges and cottages, and more importantly the fish farm in Whitefish Bay, which added ~3 500 kg of P in the 1990s.

Since the beginning of the fish farming activities, residents noticed a degradation of the water quality. The Association for the Protection of Lake Heney (APLH) filed a class action against both Truiticulture S.L. and the MEF (*Ministère de l'environnement et de la faune*) to protect the lake from more serious degradation. The APLH won its case in 1999 and the court forced the closure of the fish farm. Paradoxically, TP concentrations did not decrease after 1999 and remained around 22-25 μg/L (Carignan, 2003). During the fall turnover of November 2007, in an attempt to reduce the amount of TP, 217 tons of iron chloride (FeOOH) were distributed on Lake Heney. Since this treatment, the TP concentrations have oscillated between 8 and 20 μg/L. Although the APLH aims for a TP of ~15 μg/L, no long-term monitoring data exist for Heney Lake and there has been no study of Heney Lake's paleolimnological conditions, prior to the European settlement in the region.

Training set lakes and sampling

In order to obtain an adequate regional training set of lakes for the paleolimnological reconstruction of Heney Lake, 31 lakes including Heney were sampled. I chose this set of lakes by selecting a variety of land uses and geological units in order to span a range of trophic and chemical conditions that would hopefully be reflected in the diatom species assemblage

(Appendix I). All the training set lakes were located on the Canadian Shield, mostly on granite, gneiss, syenite and marble, and located within 80 km of Lake Heney. The surface area of the training set lakes varied from 3 to 484 hectares, with maximum depths between 1 and 53 m. All lakes were oligo-mesotrophic with TP concentrations varying between <5 and 11 μg/L, with one meso-eutrophic Lake, Lac Noir, that had a TP of 22.5 μg/L. Although all lakes had road access, little direct human development was observed, with 0 to 16 houses/km of shoreline (Appendix I).

All the training set lakes were sampled during the stratification period of 2013 and 2014. In each lake, 3-5 sediment cores were retrieved from the deepest part using a mini Glew Gravity corer (internal diameter 4 cm). In lakes Bonin and Bataille, the sediment cores were retrieved from a secondary basin. Methane bubbles from production within the sediments in lake Bonin expelled the sediments from the coring device upon retrieval at the surface. Lake Bataille was too deep for our instruments. All cores were then extruded in 0.5 cm subsections for the top 2 cm using a Glew vertical extruder. Sediment samples were placed directly into individual Whirl-Pak® sample bags or Ziploc Freezer bags and stored at -18ºC until analysis. In lake Heney, two long cores of 35 and 40 cm were retrieved with a maxi Glew Gravity corer (internal diameter 7.62 cm) on March 9, 2014, in the interest of tracking the trophic condition evolution in the past ~300 years. Both cores were extruded at 0.5 cm intervals for the top 10 cm and at 1 cm intervals below.

Subsurface water was collected at the same location and date as sediment samples. The water chemistry of whole lake water was analyzed at the City of Ottawa Water Laboratory Services using ICP-MS. The methods section in Chapter 2 provides the information on the water chemistry and physical proprieties obtained.

Dating of core and loss on ignition

To establish the core chronology, ^{210}Pb dating was performed on 16 freeze-dried subsamples from one Lake Heney core using an Ortec High Purity Germanium Gamma Spectrometer in the LANSET laboratory at the University of Ottawa. Dates and the sedimentation rate were fitted with three models: Constant Rate of Supply (CRS), Constant Initial Concentration (CIC), and Constant Flux Constant Sedimentation (CFCS). The CFCS model was chosen because of a better exponental curve fit of the ^{210}Pb activity (Binford, 1990; Appleby, 2008), using the ScienTissiME software. The ^{210}Pb dating results were confirmed with the ^{137}Cs activity values.

The loss on ignition (LOI) at 550ºC was performed on all the surface sediments samples, and on the Heney Lake sediment core. The methodology is described in chapter 2.

The iron and phosphorus concentrations in surficial sediments of the training set lakes and on the sediment core from Heney Lake were determined by ICP-MS. The methodology is described in the methods section of chapter 2.

Diatom preparation and identification

The top first centimetre of sediments in each lake of the training set, as well as 16 subsamples from the Heney Lake sediment core, were weighed, freeze-dried, and re-weighed. Subsamples of 30 mg to 55 mg were acid-digested in a 1:1 molar ratio sulfuric-nitric acid. The acid was then removed with a 5-step centrifugation dilution. Aliquots of 0.8 ml were placed on 18 mm cover slips and mounted on microscope slides using Naphrax®, a mounting medium with a high refractive index. A minimum of 600 diatom thecae per slide were identified and counted on random field using a Leica DMR compound microscope equipped with a 100x immersion oil objective and interference contrast optics (NA = 1.35). A Pixel ink® camera connected to the software Pixel Ink Capture OEM® was used to take photographs of specimens. A photo of each field counted was taken and for a homogeneous determination of the different samples, several photos of each species were taken. The individuals that were more difficult to identify were examined with a Joel JSM-6610LV scanning electron microscope at the University of Ottawa. The identification of certain species, such as *Cyclotella comensis* and *Stephanodiscus parvus*, was confirmed with Dr. Vaclav Houk (Institute of Botany, Academy of Sciences of the Czech Republic) and Paul Hamilton (Canadian Museum of Nature, personal communication). One slide per lake was counted, and an additional slide from a different core was visually inspected to ensure the consistency of diatom assemblage between cores from a same lake. On the Lake Heney core, 400 thecae were counted in each of the 16 slides prepared, corresponding to the depths used for Pb^{210} dating. Chrysophyte cysts and scales were also counted. Taxonomic references include Krammer & Lange-Bertalot (1986); Krammer & Lange-Bertalot (2000); Fallu *et al*. (2000); Lavoie *et al*. (2008); Houk, 2010.

Data analysis

A principal component analysis (PCA) was carried in R software (R Development Core Team, 2013) on the chemical and physical data of the training set lakes in order to summarize the variability and relationships between these variables, as well as to identify any potential outlier lakes. With the exception of Alk and LOI, environmental variables were either log (El, TP, TKN, Fe_d, Chl, Cond, Cal, Sec), square root (MD, HD, MP) or square (pH) transformed to obtain a normal distribution. The transformation 1/square root was applied to the variable CA: SA.

Diatom species relative abundances and Shannon-Wiener diversity index were calculated for each lake. Redundancy analysis (RDA), a constrained ordination method, was used to examine the relationships between the dominant diatom species distribution and the environmental variables, as well as to identify the variables that best described the species distribution. A forward selection procedure on the environmental variable was conducted to retain only the environmental variables that had a significant effect on the diatom species assemblage. The diatom relative abundances were transformed using the Hellinger transformation (Legendre & Legendre, 2012) while the environmental variables followed the same transformations as for the PCA. The RDA was performed on R software (R Development Core Team, 2013) using the VEGAN package.

A diatom-inferred dissolved iron transfer function for Heney Lake was developed using the program C2 version 1.7 (Juggins, 2014). Taxa that occurred in at least two of the modern samples in the training set lakes and that had a maximum abundance greater or equal to 1% of the diatom assemblage were included in the transfer function, for a total of 71 taxa. The species relative abundance data were log transformed and weighted averaging (WA) analysis was used to perform the reconstruction. This method is based on the assumptions that a species is most abundant in conditions that are optimal to its growth (ter Braak & Van Dam, 1989; Smol 2008).

3.3. Results

Training set lakes and Heney Lake environmental variables

The 30 training set lakes spanned a gradient of limnological conditions (Table 3.1). A majority of the lakes were oligo to mesotrophic, with six lakes that had TP concentrations below the detection limit (5 µg/L). The lakes with the highest TP concentrations were Lac Noir with 22.5 µg/L and Lac Guilbeault with 12 µg/L while (Appendix I). TKN values of the training set lakes also corresponded to oligo-mesotrophic conditions and varied from 190 to 570 µg/L. Because TKN was significantly correlated with TP (Appendix II), most of the lakes with TP concentrations below detection limit also had particularly low TKN concentrations (Bataille, Bonin, Gilmour, Girard, La Pêche, Pink) while Lac Noir had the highest TKN value (570 µg/L). Similarly, chlorophyll *a* was highly significantly correlated with both TKN and TP so the lakes with the lowest chlorophyll *a* values were those that also exhibited low TKN and TP concentrations and vice-versa. The chlorophyll *a* concentrations varied between 0.3 and 7.6 µg/L with a median of 2.2 µg/L. A majority of the lakes developed hypolimnetic anoxia during the stratification period. However, all lakes where the photic zone extended to the bottom of the lake, based on Secchi transparency, had oxic hypolimnion (Fraser, Létourneau, Trois Monts, Vases and Victoria). Some permanent houses and seasonal cottages were built along the shores of the lakes with a median of ~8 houses/km of shoreline. Only Pink Lake and Lac à la Perdrix had no sign of development. Lakes Pink, La Pêche and Renaud are part of the Gatineau Park, a protected area that allows only limited recreational activities like hiking, canoeing/kayaking and camping at designated sites.

Heney Lake had a larger surface and catchment surface area than any training set lakes (Table 3.1). Its TP, TKN and chlorophyll *a* concentrations were higher than the median (10.5; 345 and 3.8 µg/L, respectively) and its Secchi depth was below the median of the training set lakes (2.5 m). Similarly to the majority of the training set lakes, the hypolimnion developed anoxic conditions during the stratification period. Heney Lake's water also had relatively high pH and alkalinity values (8.8 and 88.3 meq/L). About 150 houses and cottages were built along its shore, with slightly higher building density than the media of the other lakes (5.8 buildings/km of shoreline).

The organic matter content was relatively high in surficial sediments for a majority of the training set lakes, as indicated by the LOI values (table 3.2) with an average of 43%, except Lake Bitobi (7.75%). Lake Heney had a relatively low organic matter concentration compared to the training set lakes with a LOI value of 20%. Chrysophyte cysts and scales were present in a majority of the training set lakes, reaching as much as 1 cyst and 1 scale for every 4 diatom valves in Lake Girard. In contrast, a few lakes had no chrysophyte scales and very little cysts (La Pêche, Renaud, Trois Monts, Victoria).

The PCA based on the chemical and physical data of the training set lakes suggested no outlier lakes. Eigenvalues of the first (λ_1= 0.29) and second (λ_2= 0.23) axes accounted for 52% of the variation in the environmental data (Fig. 3.1). The variables with the highest loadings for the first principal component were pH (-0.358), Secchi depth (0.349), dissolved iron (0.352), and the catchment to lake area ratio (-0.319) (Appendix VII). As for the second component, the main contributors were TKN (-0.395), calcium concentration (-0.363), maximum depth (0.360) and conductivity (-0.354). As expected, related variables such as chlorophyll *a*, TP and TKN; in addition to percent marble of the catchment, alkalinity, conductivity, calcium concentration and pH were grouped on the PCA biplot, which indicates correlation between these variables (Fig. 3.1).

Trends in diatom composition across lakes

I identified a total of 316 diatom species of 64 genera. On average, each lake had 45 species in surficial sediments. Of these, 2 to 7 species had an abundance over 5% in each lake. Among the training set lakes, Shannon's diversity index varied from 1.19 (Lac Pink) to 3.24 (Lac Bonin) with a median of 2.55 (Lac Demi-Lune) (Table 3.2). Dominant taxa in the training set included *Cyclotella comensis*, *Staurosira construens*, *Staurosira construens var. venter*, *Cyclotella stelligera*, *Fragilaria crotonensis*, *Tabellaria flocculosa*, *Aulacoseira subarctica* and *Asterionella formosa* (Fig. 3.2 and Fig. 3.3). In the majority of lakes, centric diatoms (mainly the genera *Cyclotella*, *Aulacoseira* and *Stephanodiscus*) represented about 50% of the diatom composition, such as in lac Vert (Appendix IX), Perdrix, Pink and Heney. *Cyclotella* spp. dominated over *Aulacoseira* in all of the lakes except in lakes Jean Venne and Loups where *Aulacoseira* spp. were more abundant. Lakes that were rather dominated by benthic diatoms were among the shallowest ones (Létourneau, Renaud (Appendix X), Trois Monts), with *Staurosira construens*, *Staurosira construens var. venter*, *Pseudostaurosira brevistriata* and *Staurosirella pinnata* dominating.

The forward selection in the RDA identified three environmental variables (maximum depth (MD), percent marble (MP) and dissolved iron (Fe_d)) that explained significant ($p < 0.05$), independent direction of variation in the diatom taxa (Fig. 3.4). Although TP did contribute to the model significance and was independent of the other retained variables, its contribution was not significant (p-value = 0.14). Therefore, any further analysis with this variable must be used with precaution and robust conclusions cannot be made concerning with this variable. The RDA axis 1 (λ_1= 0.16) and axis 2 (λ_2= 0.13) were both significant and explained 29% of the variance of the diatom species variation in the training set lakes. Among the four explanatory variables, maximum depth (MD) had the strongest relationship with the primary axis (loading = -0.92; Appendix VIII). Relatively deep lakes (Profond, Orignal, Perdrix, Twin, Girard, Bataille, Gilmour) tended to have their diatom assemblage dominated by *Cyclotella stelligera*, *Tabellaria flocculosa* and *Asterionella formosa* (Fig. 3.3 and 3.4). The second variable that contributed most to the first axis was percent marble in the catchment (MP) (loading = -0.40), followed by dissolved iron (loading = 0.39). The centric diatom *Cyclotella comensis* dominated lakes with an important proportion of marble content in their catchment (Bitobi, Gervais, Heney, Truite; Fig. 3.4). TP had a loading of 0.28 on the first axis but again, was not significant.

Heney Lake sediment core

The sediment core extracted from Heney Lake in March 2014 was 40 cm long. The surficial sediments contained rusty-brown material (Appendix XI A). The top 26 cm consisted of loose sediments, while the lower portion was clay-rich and dense (Appendix XI B). The ^{210}Pb activity trend followed a characteristic exponential decline through depth, suggesting that sediment mixing was not an issue in the sediment core (Appendix VI). A distinctive ^{137}Cs peak was apparent between the 4 and 5 cm depth, corresponding to between ca. 1975 and 1958 based on the Constant Flux Constant Sedimentation Rate (CFCR) model. Extrapolation of the resulting ^{210}Pb chronologies using the CFCR model indicated that the sediment core spanned ~1180 years, from the time of sampling (2014) to ca. 834 CE for the bottom of the core. However, the sediments below 11 cm (ca. 1789 CE) fall beyond the half-life decay limits of the ^{210}Pb dating and therefore, the dating is not reliable below this depth. The CFCR model assumes a constant sedimentation rate, which was estimated as 0.0119 (±9 e^{-4}) $g/cm^2/y$. This sedimentation rate was validated with the CRS model, which does not assume constant sedimentation. The sedimentation rates calculated with the CRS model varied from 0.0092 (±0.0027) to 0.0124 (±0.0009) $g/cm^2/y$, which includes the rate suggested by the CFCR model.

A total of 133 diatoms species were identified throughout Heney Lake sediment core from 43 genera, with 13 species representing >5% abundance in at least one subsample. Of all the taxa identified in the core, 105 were also identified in the training set lakes. A majority of the dominant taxa in the Heney Lake core were also dominant in many lakes of the training set: *Cyclotella comensis*, *Fragilaria crotonensis* and *Tabellaria flocculosa*. Some dominant species in the core were present in the training set although not dominant, including *Aulacoseira subarctica*, *Stephanodiscus medius* and *Cyclotella bodanica*. Surficial sediments of Heney Lake had a relatively low Shannon diversity index with a value of 1.79. However, the diversity index was higher in deeper sediments (Fig. 3.6).

Changes occurred in the diatom species assemblage through the core, with particular changes above the cm 11 (ca. 1789). In the deeper portion of the core (40 – 10 cm), *Aulacoseira subarctica* was the dominant species, representing 27-45% the diatom assemblage. Other prominent species included *Aulacoseira ambigua* (2-11%), *Cyclotella bodanica* (4-6%), *Stephanodiscus medius* (2-11%), *Tabellaria flocculosa* (5-14%) and *Staurosira construens* (0.25-7%) (Fig. 3.5 and Appendix XI D). In the period between 3 and 10 cm (ca. 1989 CE to ca. 1789 CE), there was a significant increase of *Cyclotella comensis* (7 to 20%) as well as a gradual increase in *Fragilaria crotonensis* (11-15%). The sharp rise in *Cyclotella comensis* was accompanied with a decline in *Aulacoseira subarctica*, which nonetheless remained the most abundant species (20-38%). The species *Stephanodiscus vestibulis* and *Staurosira construens* also declined and were almost absent during that period. In the top portion of the core (<3 cm), *Cyclotella comensis* further increased and became the dominant species (25 to 42%) in conjunction with a decline in *Aulacoseira subarctica*, which became the second most dominant taxa (17-30%) (Appendix XI C). *Fragilaria crotonensis* became the third most abundant species

(20-24%). *Aulacoseira ambigua* was absent from that stratum although it represented 2 to 10% of the assemblage down core, whereas *Stephanodiscus vestibulis* and *Staurosira contruens* remained absent. Other species like *Cyclotella bodanica* (2-6%) and *Tabellaria flocculosa* (4-14%) remained relatively constant throughout the entire core.

The centric diatom *Stephanodiscus parvus* was not among the most abundant species in Heney Lake, yet shows an interesting stratigraphy. This species was nearly absent throughout the pre-European settlement period and increased at the 9th cm (ca. 1862 CE) to reach a maximum of 3.5% in the 3rd cm (ca. 1989 CE; Fig. 3.10). The relative abundance of this small centric diatom then oscillated between 1.5 and 2.3% in the sediments < 3 cm.

The significant increase in *Cyclotella comensis* and other *Cyclotella* species in the upper portion of the sediment core was synchronous with changes in the planktonic: benthic diatoms ratio (Fig. 3.6). During the pre-European settlement period (>10 cm), the diatom community was composed of ~11-35% of benthic/thychoplanktonic diatoms such as *Fragilaria capucina*, *Ulnaria ulna* (previously *Synedra ulna*) and *Fragilaria* spp. In the period from 10 to 3 cm, the planktonic: benthic diatoms ratio increased and benthic species occupied ~8-12% of the total diatom assemblage. The most recent sediments (<3 cm) exhibit the highest planktonic: benthic ratio, and the previously abundant benthic species were almost absent. The organic matter content, as expressed by LOI, was stable (~7-9%) during the pre-European settlement period. From 10 to 3 cm, LOI gradually increased and continued to rise in the uppermost sediment layers, reaching a maximum of 20% in surficial sediments.

Chrysophytes cysts and scales were present throughout the core of Heney Lake, yet in relatively small amounts (Fig. 3.6). I counted ~3-15 cysts/100 diatom valves and 0-2 scales/100 diatom valves during the pre-European settlement period. The number of cysts was relatively stable in the post-European settlement period with ~3-6 cysts/diatom valves (x100), while the number of scales varied from ~0-1.6%.

Because TP was not retained as a significant driver of the diatom species community in surficial sediments of the training set lakes, I was unable to conduct a reconstruction of this variable in the

Heney Lake sediment core. However, dissolved iron (Fe_d) had a significant effect on the diatom species assemblage (Fig. 3.4), which allowed for the reconstruction of this variable throughout the sediment core. Table 3.3 shows the results of the selected inference model obtained using weighted averaging with inverse deshrinking. All lakes were included in the transfer function and a $\log_{10}$ transformation was applied to the chemistry data. The selected model had an $R^2_{apparent}$ of 0.51 while the R^2_{boot} was 0.17. The root of the mean squared prediction error (RMSEP) was 2.92 µg/L with a maximum error of 7.30 µg/L and a mean error of 1.07 µg/L. The model covers a Fe_d gradient of 0.7 µg/L to 114.25 µg/L, so the RMSEP equates to ~2% of the Fe_d gradient. The inferred dissolved iron concentrations were relatively constant below 18 cm (ca. 1549 CE), between 9.1 and 15 µg/L (Fig. 3.8). A decline in the iron concentrations started prior the European settlement and remained between 5.8 and 8 µg/L from ca. 1649 to ca. 1989 CE. A sharp decline occurred concomitantly to the fish farming activities, between the 5th (ca. 1989) and the 4th cm (ca. 1999), with iron concentrations dropping to 3 µg/L. Iron remained at the lowest concentrations of the entire core in the upper sediments (< 4 cm), oscillating between 3.2 and 3.5 µg/L. A small short-time increase occurred in the 1st cm of the core, which corresponds to the iron treatment in Heney Lake (2007), during which the inferred iron concentrations reached 4.8 µg/L.

The measured iron to phosphorus ratio in the Heney Lake sediment core has decreased slightly from old to recent sediments (Fig. 3.9). During the pre-European settlement period (> 10 cm), the Fe: TP ratio (by weight) oscillated between 20 and 14. After the European settlement in the Outaouais region, the Fe: TP gradually decreased and reached < 10 in surficial sediments. The Fe: TP ratio in the 30 training set lakes varied between 1.5 and 21, with an average of 10. Therefore, the surficial sediments of Heney Lake have about the same Fe: TP ratio as the average of the other 30 study lakes.

3.4. Discussion

Reconstruction of Heney Lake trophic conditions

The sediment core from Heney Lake used to reconstruct the paleolimnological conditions was 40 cm long and represented material deposited since ca. 834 CE, based on ^{210}Pb dating. However, the data below 11 cm fall beyond the half-life decay limits of the ^{210}Pb dating and so the dating is only reliable for sediments above this depth. The estimated sedimentation rate was 0.0119 (±9 e^{-4}) g/cm^2/y; this is comparable to other lakes in the vicinity. For example, Pal et al. (2015) found sedimentation rates between 0.001 to 0.037 g/cm^2/y in five lakes of the Outaouais region including lake La Pêche. As the main objective of this study was to quantify changes in limnological conditions since the European settlement in the Outaouais region (ca. 1800-1850), and to set the approximate nutrient conditions prior to significant anthropogenic disturbance, I focused on the material that represented the period between the arrival of Europeans and the present. This period also corresponds to the reliable results of ^{210}Pb dating.

A premise of this study was that diatom communities in Heney Lake would have changed since European settlement, especially in the XXth century, primarily in response to changes in the nutrient conditions. The RDA indicated that neither TP nor TKN was a significant driver of the diatom species community in the training set surficial sediments (Fig. 3.4) and therefore, a reconstruction of nutrient conditions was not possible. This was surprising as diatom communities are known to respond to changes in the nutrient conditions and have therefore been used in a large number of paleolimnological reconstructions (e.g. Tremblay et al., 2014; Hadley et al., 2013; Rühland et al., 2010; Smol, 2008; Rühland et al., 2008; Anderson et al., 1994). The lack of significancy between nutrients and the diatom assemblage was probably due to the lack of meso-eutrophic lakes in the training set. Seven of the training set lakes had a TP concentration below the detection limit (5 µg/L), 22 lakes had a TP between 5 and 10 µg/L, and only one lake (Noir) had a TP above 15 µg/L (Appendix I). Therefore, only one lake (Noir) had a current TP concentration superior to Heney Lake (10 - 17 µg/L). An important aspect of building a transfer function is the selection of a suite of training set lakes that span the range of TP conditions that one is likely to encounter in the limnological history that one wishes to reconstruct (Smol, 2008). Because Heney Lake's present instrument-measured TP is higher than all other training set lakes (except Lac Noir) any event of increasing TP conditions to higher values than actual ones in the history of Heney Lake would likely not be captured by the transfer function. The region likely contains few eutrophic lakes so this problem would not be solved by sampling more lakes.

Although the overall diatom community in the training set lakes of the Outaouais region was not adequate to perform a TP reconstruction in Heney Lake, certain specific diatom species may be used to infer changes in the nutrients status of the lake. More specifically, the small benthic diatom *Stephanodiscus parvus* has commonly been associated with lake eutrophication in paleolimnological studies (e.g. Berthon et al., 2014; Heinsalu et al., 2007; Rusak et al., 2004; Hyatt et al., 2001; Interlandi et al., 1999). This small planktonic species is commonly found throughout Europe and North America in meso-eutrophic lakes during early stratification (Berthon et al., 2014). Because of its small size (<12 μm) and thin frustule, this centric diatom flourishes at high P availability (Heinsalu et al., 2007). For example, in a paleolimnological study of Minnesota lakes, Ramstack et al. (2003) found that the TP optimum of *S. parvus* was 42 μg/L in their 55 training set lakes. It is also a strong competitor for Si and can therefore dominate in low Si: P ratios (Heinsalu et al., 2007).

In the Heney Lake sediment core, *S. parvus* was absent from the diatom community prior to European settlement (Fig. 3.11). A few individuals were identified in the 9th cm layer of the sediment core (ca. 1862), which corresponds approximately to the beginning of the development in the Outaouais region. Indeed, it was in the 1820s, with the construction of the Rideau Canal, that the forest industry on the north side of the Ottawa River began (Messier, 2007). The logging activities were intensified with the Reciprocity Treaty in 1854, a trade treaty between Great Britain and the United States that also applied to other British possessions including the United Province of Canada. The rapid development of cities in the United States increased the demand for Canadian timber and in order to meet the increasing demand, forest clearing expanded towards the north in the Gatineau River valley as far as Maniwaki (50 km north of Heney Lake; Messier, 2007). Forest clearing, and the subsequent soil scarification and erosion, can lead to the reduction of nutrient intake by the land vegetation and therefore to the increase in both the inorganic and organic load from the catchment to the lake, which stimulates phytoplankton growth and may lead to cyanobacteria blooms (Rask et al., 1998). In a study of 13 Québec lakes where significant forest clearing was done in the watershed, Carignan et al. (2000) found that dissolved organic carbon and the light attenuation coefficient were up to threefold higher in forest cut lakes than in reference lakes, while TP and total inorganic nitrogen were two to three-fold higher than non-impacted lakes. Therefore, the increase in *S. parvus* relative abundance starting in ca. 1862 was likely due to the forest clear-cutting during this period.

The relative abundance of *S.parvus* rose abruptly between the 4th (ca. 1914) and 3rd cm (ca. 1989) of sediments to reach a maximum relative abundance of ~3.5% in the 3rd cm (Fig. 3.10). This period was characterized by a continuation of the logging industry in the Gatineau River Valley that had started during the previous century, but also by the building of houses, cottages and fishing and hunting lodges. As mentioned earlier, the first cottage along the shore of Heney Lake was built in 1902 and the first fishing and hunting lodge opened in 1925 (Gatineau Lakes Heritage, 2010). The development continued in the 1920s and subsequently. The building of houses and cottages was also a potential source of nutrient inputs to the lake as it involves tree clearing, landscaping work, the use of fertilizers for lawns and gardens, and the use of P-rich detergents (P in detergents were only prohibited in Québec in 2010; Government of Québec, 2010). Therefore, the logging industry in the watershed in combination with the residential development might have increased significantly the amount of nutrient exports to Heney Lake, which would have allowed *S. parvus* to thrive.

Similarly to *S. parvus*, the planktonic species *Fragilaria crotonensis* has also been associated with lake eutrophication (Heisalu et al., 2007). This species represented ~1.4-3% of the diatom assemblage prior to the European settlement (Fig. 3.5). With a similar trend as *S. parvus*, the abundance of *F. crotonensis* gradually rose in the period from cm 9 (ca. 1862) to 3 (ca. 1989) and reached a maximum in the 2nd cm of sediments (ca. 1999). The logging industry in the Outaouais region, including in Heney's watershed as well as house/cottages building along the shores were concomitant with the rise in *S. parvus* and *F. crotonensis*. Moreover, a significant increase in the organic content occurred in the last century (Fig. 3.6). From the bottom of the sediment core to the 5th cm (ca. 1958), LOI values varied between 7.7 and 9.7%. The LOI values constantly increased afterwards and reached a maximum of 20% in the surficial sediments. The rise in *S. parvus* and *F. crotonensis*, added to the increase in the sediment organic content, likely reflects the onset of human-induced disturbance of the ecosystem and an increase in the overall lake productivity, beginning in the late XIXth century with an acceleration during the ~1960s. Similar trends of increasing relative abundance of *S. parvus* and *F. crotonensis* concomitant to the increase in nutrient loading were observed in Lake Bourget, France (Berthon et al., 2014). Increases in *S. parvus* were also observed throughout Lake of the Woods (Ontario) in modern sediment samples compared to pre-industrial sediments (Hyatt et al., 2011). Increases in organic content were characterized in sediment cores from lakes Laurie and Woodcock (central British Columbia), both impacted by forest clear-cutting (Laird et al., 2001).

Some effects of the recent human activities on Heney Lake may also include a decline in the diatom species diversity. The diatom diversity index was higher prior to European settlement, with a Shannon diversity index varying between 2.5 and 2.8, while most recent sediments had an index below 2 (Fig. 3.6). In comparison, Thies et al. (2012) found a mean Shannon diversity index of 2.9 for the first 10 cm of a sediment core from Piburger See in the Tyrol region, Austria. This lake showed signs of moderate eutrophication during the 20th century, followed by a slow re-oligotrophication since the mid-1980s because of lake retoration.

The effect of the fish farm in Heney Lake

When the fish farm began its activities (1993 to 1999), residents rapidly noticed a water quality degradation which they thought was caused by the aquaculture (Carignan, 2003). Fish farming and other aquaculture operations have been linked to numerous environmental effects including nutrient enrichment, habitat alteration, changes in dissolved oxygen, and damage to wild fish populations (Gross, 1998). The large amounts of nutrient-rich feed used for the harvest fish generate important quantities of waste from the uneaten feed, as well as metabolic wastes (urine and faeces). Faecal production typically represents 15-30% of applied feed (Cho & Bureau, 2001) while waste feed varies between 4% and 40% of applied feed (Weston et al., 1996). The primary concerns associated with this waste generation are nutrient enrichment and reductions in hypolimnetic dissolved oxygen concentrations (Fisheries and Ocean Canada, 2006). Dissolved carbon, nitrogen and phosphorus can solubilize in the water column from the excessive feed and faeces (Bureau & Cho, 1999), where they may stimulate algal blooms. Ackefors and Enell (1994) estimated that the production of one metric ton of fish releases 3 to 10 kg of P and 39 to 55 kg of N in the environment. A significant portion of the solid wastes settles to the surface of sediments and the greatest accumulation of P, N and organic C occurs directly under the fish cages (Kelly, 1993; Troell & Berg, 1997), suggesting that direct effects on sediments may be geographically restricted (Fisheries and Ocean Canada, 2006). Furthermore, decomposition of the organic wastes consumes oxygen and may lead to significant decreases in hypolimnetic dissolved oxygen concentrations (Fisheries and Ocean Canada, 2006).

Even though the training set did not allow for the reconstruction of TP conditions in Heney Lake, the nutrient-enrichment associated diatom species *Stephanodiscus parvus* (e.g. Berthon et al., 2014) had been occupying an increasing portion of the diatom assemblage well before the fish farming period (Fig. 3.10). In fact, the relative abundance of this small centric diatom increased rapidly in the period between the 5th (ca. 1958) and the 3rd cm (1989). Afterwards, the counts ironically decreased during between the 3rd (ca.1989) and 2nd cm (ca. 1999), which corresponds to the aquaculture period, then gradually increased again until present. Similarly, *Fragilaria crotonensis*, which has also been associated with lake eutrophication (Heisalu et al., 2007), has been accounting for an increasing proportion of the diatom assemblage since the XIXth century (Fig. 3.5). However, the counts of this species kept on increasing during the fish farming period, contrarily to *S. parvus*. The trend in these two specific planktonic diatoms suggests Heney Lake has been experiencing nutrient enrichment before the aquaculture started its activities in 1993. Nutrient enrichment probably began in the mid 1900-1950s. In the Gatineau River Valley region, this period corresponds to the onset of the logging industry. More specifically, many houses, cottages and fishing and hunting lodges were being built along the shores of Heney Lake. These activities certainly increased the nutrient load into Heney Lake, which translated into changes of the diatom assemblage, with the rise of both *S. parvus* and *F. crotonensis*.

Dissolved iron concentrations in the training set lakes were significantly correlated with the diatom assemblage, which allowed for a reconstruction of this variable (Fig. 3.4; Appendix VIII). One other study also found that dissolved iron helped explain the diatom community in surficial sediments across 55 southern Québec Lakes, east of the Outaouais region (Tremblay et al., 2014). In a canonical redundancy analysis (RDA), the authors identified 19 environmental variables that explained a significant portion of the diatom assemblage in their training set lakes, among which iron was retained, along with TP, pH, conductivity, alkalinity and the nitrogen to phosphorus ratio, notably. Although the effect of dissolved Fe on the diatom assemblage was ~3 times less important than the effect of TP and the nitrogen to phosphorus ratio, these were in the same direction. Few diatoms training sets include iron in their analyses so the importance of this factor has not been formally addressed (Enache & Prairie, 2002). In river and stream ecosystems, Larson et al. (2015) found that iron was a major driver of algal dynamics, including diatom biodiversity: using algal abundance in microcosm experiments and water chemistry data from the National Water-Quality Assessment Program in the United States, the authors determined community threshold along iron gradients for non-acidic running waters: 30-79.5 μg/L and 70-120 μg/L for oligotrophic and eutrophic streams, respectively. Iron concentrations below these thresholds caused distinct shifts and deleterious effects in the phytoplankton communities. As 50-75% of sampled streams in the US fall below these thresholds, iron limitation is potentially wide-spread in North America which the authors interpreted as the result of the limited distribution of wetlands, which are a major Fe source for streams. Also, Passy (2010) found that Fe was among the strongest predictors of diatom richness in a latitudinal study of 531 streams in the United States.

Interestingly, the DI-Fe was relatively high in the sediments >11 cm (ca. 1789) (20 - 30 μ/L, Fig. 3.8) compared to measured values of the lake surface water at the time of sampling (Appendix I). Concomitant to the European settlement, the DI-Fe gradually decreased and showed little variation until ca. 1989. A significant and abrupt decline then occurred between ca. 1989 and 1999, corresponding to the fish farm period. The inferred Fe concentrations gently increased again at 1 cm depth (ca. 2007), to then decrease until the most recent sediments.

This particular pattern in the DI-Fe concentrations suggests the fish farm may have indirectly affected the iron concentration in Heney Lake. A possible mechanism is that the fish farm would have added nutrients to the lake, mainly through the feed to harvest fish, as well as faeces and the accumulation of uneaten feed. The excessive P would have bounded to the Fe contained in the water column and then sank to the bottom of the lake to remain in the sediments, as the complex formed by Fe^{3+} and P is insoluble (e.g. Mortimer, 1942). In other words, the P added by the fish farm was rapidly taken up by Fe in the water column, which reflected in a decrease of the DI-Fe. The fish farm would have therefore “consumed” the iron in Heney Lake. The source of Fe for lakes is typically through the water-bedrock interaction, within the lake and in its watershed (e.g. Xing & Liu, 2011). Heney Lake and half of its watershed lies on marble, as opposed to a majority of lakes of the Canadian Shield. This carbonate rock contains little amounts of Fe, and therefore, receives limited of this element from its catchment. Carignan (2003) in fact suggested that Heney Lake is Fe-limited, a situation likely due to natural causes (i.e. bedrock composition), but aggravated by the fish farm. Our results support this hypothesis, as the DI-Fe significantly dropped in the sediment layer corresponding to the fish farm period.

In order to reduce the TP concentrations in Heney Lake, the Association for the Protection of Lake Heney (APLH) proceeded with an iron treatment in November 2007, during which they spread 217 tons of iron chloride evenly on the lake surface. Our DI-Fe reconstruction shows an ephemeral increase in Fe concentration during this year (Fig. 3.8). However, the Fe concentration later declined to similar levels as during the fish farming activities, the lowest described by our reconstruction. This suggests there are still important sources of P to the lake that surpass the amount of Fe that Heney Lake receives from its interaction with the bedrock and its watershed, which is supported by the real-time instrument-measured TP values since the Fe treatment: the Fe treatment instantly decreased the amount of TP, but the concentrations increased again during the following seasons (Appendix V). In comparison with the other study lakes of the training set, Heney Lake has among the lowest values of real-time measured epilimnetic Fe (Appendix I).

Similarly to the DI-Fe trend, the measured sediment Fe: TP ratio has gradually been decreasing over time (Fig. 3.9). During the fish farm period, the Fe: TP did drop, but this trend had started earlier. As opposed to the diatom-based reconstruction, the measure of Fe: TP in the sediments did not capture a change with the iron treatment. However, these elements are highly mobile in the sediment-water interface as redox conditions change rapidly. Also, the Fe added to the lake may have been affected by bioturbation and diagenesis processes (Carignan, 2013).

Climate change

In Lake Heney sediment core, a shift from *Aulacoseira* spp. (mainly *subarctica*) to *Cyclotella* spp. (mainly *comensis*, with some *bodanica*, *distinguenda* and *ocellata*) was observed in recent sediments (Fig. 3.5 and 3.6). Below 11 cm and prior to the mid 1800s, the dominant diatom species was *A. subarctica*, representing 29 to 45% of the total diatom assemblage while *C. comensis* represented 0 to 3 %. As *A. subarctica* gradually declined in upper sediments, *C. comensis* rapidly occupied an increasing proportion of the diatom community and reached 42% of relative abundance in the surficial sediments (Fig. 3.5), representing ~70% of the planktonic species. Moreover, the ratio of planktonic: benthic diatom species was stable at a ratio of ~ 8 in the deeper section of the sediment core (>10 cm), and started rising gradually at 9 cm (ca. 1862), to then rise abruptly in the 3rd cm (ca. 1989) (Fig. 3.6). In recent sediments, the ratio of planktonic: benthic diatom species was ~ 40, which represents a 5 fold increase from pre-European settlement values.

Such an expansion of *Cyclotella* spp. is consistent with several other studies performed on other oligo-mesotrophic lakes of arctic, subarctic and temperate regions throughout the world, both in sediment cores and in phytoplankton samples (Tolotti & Thies, 2002). Similar trends were even observed in deep lakes of Baffin Island, Svalbard, Scandinavia, and the western subarctic region of North America (Smol et al., 2005). In a review of 105 lakes that were not significantly impacted by direct human disturbance or acid deposition (TP < 20 μg/L and pH > 6), Rühland et al. (2008) found that 80% (84 lakes) showed a >5% increase in the relative abundance of *Cyclotella* species since the mid 19th century. The study lakes were dispersed in North America, Europe and Scandinavia, and included temperate, Arctic and alpine lakes. The authors attributed the widespread major shift from *Aulacoseira* spp. to small *Cyclotella* spp. to climate change. Several other studies have come to similar conclusions (Rühland et al., 2008). In Lake of the Woods (Ontario), the clear increase in small *Cyclotella* spp. with the concurrent steep decline in *Aulacoseira subarctica*, beginning ca. 1980, closely tracks a sharp rise the temperature recorded at the nearby Kenora weather station (Rühland et al., 2008). The positive relationship observed between the temperature record and the changes in the diatom community composition provide strong evidence that the warming trend observed in the past decades has an important impact on the diatom community structure.

Additionally, regional trends from 50 lakes in central subarctic Canada, where the most important climate warming of North America was documented (Rühland et al., 2003), also show a significant shift from benthic to planktonic dominance of diatom species (Smol et al., 2005). In subarctic regions of Finland, recent increases in the relative abundances of small *Cyclotella* species were concurrent with decreases in *A. surbarctica* and again, this shift was associated with warming-related changes (Sorvari & Korhola, 1998; Sovari et al., 2002). In the Ottawa-Gatineau, historical records show that in general, the annual mean temperature has not increased significantly since the late XIXth century (Leblanc et al., 2008). However, the mean diurnal range (difference between daytime and night time temperatures) decreased from 10-12ºC at the beginning of the XXth century to 9-10ºC at the end of the century. Also, the number of cold years has decreased over the same period (Leblanc et al., 2008). The diatom species shift observed in the Heney Lake sediment core may be related to these changes and the current trend will likely continue as summer air temperatures are anticipated to rise by 3ºC by 2040 (Leblanc et al., 2008).

Many phenomena related to climate change can impact the diatom species assemblage in temperate lakes, including changes in temperature, the length of ice-free periods, the timing, duration and strength of thermal stratification, increased solar radiation (Tadonleke et al., 2009) and changes in wind regimes (Berthon et al., 2014). The small size and the circular shape, as well as a relatively fast growth rate of *Cylotella* species (Rautio et al., 2000) is thought to increase their competitive ability in stratified and nutrient-poor water (Winder et al., 2009). *C. comensis* is favoured when the growing season is lengthened, spring overturn is extended, hypolimnetic waters are warmer and when water stability is strengthened (Rautio et al., 2000; Sorvari et al., 2002; Rühland et al., 2003). In contrast, *A. subarctica* has a particularly thick silicified cell wall, which reduces its buoyancy (Appendix XII). This species therefore requires strong and sustained turbulence in order to maintain their position in the water column (Kilhmam et al., 1996).

In the Heney Lake sediment core, the increased contribution of *C. comensis* to the total pelagic diatom community, synchronous with the decline of *A. subarctica*, is likely due to some climate change effect. The lake may have become a more suitable environment for *C. comensis*, because of, for example, warmer temperatures, longer stratification periods and modifications in the wind regimes, which result in a more stable water column and the deepening of the epilimnion. Similarly to Heney Lake, *Cyclotella* spp. dominated over *Aulacoseira* spp. in recent sediments of a majority of the training set lakes (Fig. 3.11). The few exceptions were the very shallow lakes such as Renaud (5 m), Trois Monts (1 m) and Létourneau (4 m). The timing of the major shift in Heney Lake, ca. 1960, is similar to what was observed in many Ontario lakes at similar latitudes (Rühland et al., 2008). Although the degree of ecological response varies between lakes, probably due to variations in morphological and limnological conditions, the similarity in the diatom trend, with a strong shift from benthic to planktonic species and from the heavily silicified *Aulacoseira* spp. to small *Cyclotella* spp. over the XXth century is striking and Heney Lake falls exactly in this trend.

Interestingly, the most significant change to Heney Lake in the past 200 years may be from climate change, as indicated by the shift in the diatom community from *Aulacoseira* spp. to *Cyclotella* spp. (mainly *C. comensis*). This specific shift is also observed in a large amount of lakes within temperate, arctic and subarctic lakes of North America and Europe. This common trend provides a portrait that climate-driven, species-specific changes are now obvious across a wide spectrum of lakes, which may also be a distinctive biostratigraphic indicator of the Holocene-Anthropocene transition.

Table 3.1 Summary environmental characteristics for the 30 training set lakes. The measured range of values for each variable is shown, with the median given in parentheses.

	Training set	Heney Lake
Number of lakes	30	
Elevation (m)	124 - 237 (171)	144
Lake surface area (ha)	3 - 1231 (32)	1231
Catchment area (ha)	14 - 7867 (1569)	7867
Maximum depth (m)	1 - 53 (15)	34
House density (# houses/km shoreline)	0 - 16 (6)	8.8
pH	6.75 - 8.74 (8.12)	8.62
Conductivity (µS/cm)	44 - 243 (132)	132
TP (µg/L)	BD* - 22.5 (6.5)	10.5
TKN (µg/L)	190 - 570 (310)	345
Calcium (mg/L)	5.7 - 40.8 (19.4)	19.4
Secchi depth (m)	1.2 - 8.6 (4.2)	2.5
Bottom DO (mg/L)	<1 - 11.46 (<1)	< 1
Alkalinity (meq/L)	15 - 170 (78)	88.3
Chlorophyll a (µg/L)	0.3 - 7.6 (2.2)	3.8

*BD= below detection (5 µg/L)

Table 3.2 Main characteristics of the diatom and chrysophyte communities of surficial sediments in the training set lakes and Heney Lake, as well as the organic content (LOI).

Lake	# of diatom species	Shannon Wiener Diversity index (H)	Species evenness	Chrysophyte cysts/diatom (x100)	Chrysophyte scales/diatom (x100)	Planktonic : Benthic diatom ratio	Surficial sediment LOI (%)
Bataille	55	2.89	0.72	11.26	0.65	4.56	46.53
Bell	52	2.61	0.66	9.92	1.63	1.83	39.00
Bernard	42	2.49	0.67	10.06	1.60	6.59	36.11
Bitobi	57	2.02	0.50	7.25	2.97	8.28	7.75
Bob	45	2.14	0.56	1.98	2.15	2.52	51.15
Bonin	85	3.24	0.73	16.30	13.79	1.17	40.74
Demi-Lune	41	2.55	0.69	2.88	0.16	0.04	69.11
Eau Claire	33	1.65	0.47	2.55	0.10	0.07	39.31
Fraser	17	1.63	0.57	1.50	0.17	0.10	59.69
Gervais	53	2.62	0.66	8.07	2.97	4.95	30.46
Gilmour	44	2.78	0.73	15.75	0.33	3.40	34.39
Girard	63	2.94	0.71	25.29	30.08	6.00	39.74
Guilbeault	61	3.19	0.78	6.62	17.61	0.93	56.96
Heney	**18**	**1.79**	**0.62**	**5.45**	**1.49**	**9.27**	**20.44**
Jean Venne	50	2.82	0.72	18.15	0.49	1.77	40.11
Kalalla	54	3.04	0.77	23.00	1.14	2.57	60.10
La Pêche	64	3.19	0.77	7.84	0	0.71	48.45
Letourneau	47	2.21	0.57	0.65	1.14	0.07	24.16
Loups	55	3.13	0.78	7.59	0.83	2.10	32.39
Noir	48	2.73	0.71	8.77	0.83	4.60	24.76
Orignal	48	2.50	0.64	17.27	4.93	11.47	64.16
Perdrix	42	2.43	0.65	9.23	1.56	12.04	31.23
Pink	32	1.19	0.34	2.49	3.65	7.69	50.49
Profond	36	2.64	0.74	3.30	13.84	4.09	36.95
Renaud	60	2.81	0.69	2.38	0	0.13	50.83
Trois Monts	28	1.73	0.52	0.14	0	0.01	68.40
Truite	29	1.81	0.54	7.41	1.48	4.84	46.67
Twin	43	2.46	0.65	2.94	18.27	5.17	19.52
Vases	61	2.92	0.71	0.33	0	0.28	83.60
Vert	30	1.50	0.44	2.98	2.65	21.62	46.35
Victoria	28	1.64	0.49	0.99	0	0.02	32.69
Average	45.84	2.43	0.64	7.75	4.08	4.16	43.00

Table 3.3 Performance statistics for the best performing inverse weighted averaging model (WA_Inv) for the reconstruction of dissolved iron (Fe_d) in Heney Lake.

No. of lakes	30	
No. of taxa	71	
Gradient	0.7 – 114.25 μg/L	
	Log10	μg/L
$R^2_{apparent}$	0.51	-
Mean error	9.22E-16	1.00
RMSE	0.3362	2.17
R^2_{boot}	0.1682	-
Mean error	3.07E-02	1.07
Max error	0.8634	7.30
RMSEP	0.4656	2.92

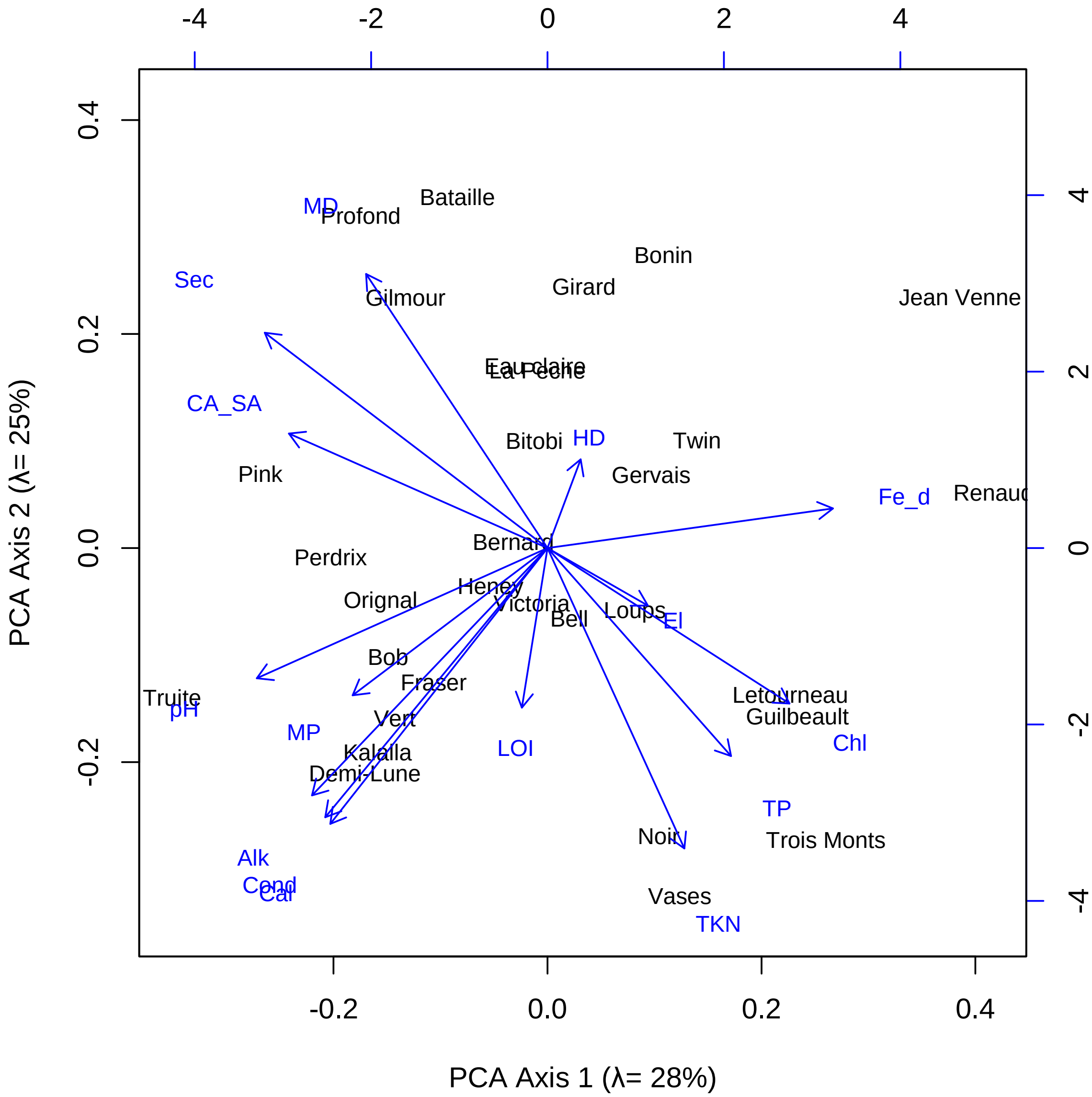

Figure 3.1 Principal component analysis biplot of environmental variables in the 30 training set lakes and Heney Lake.

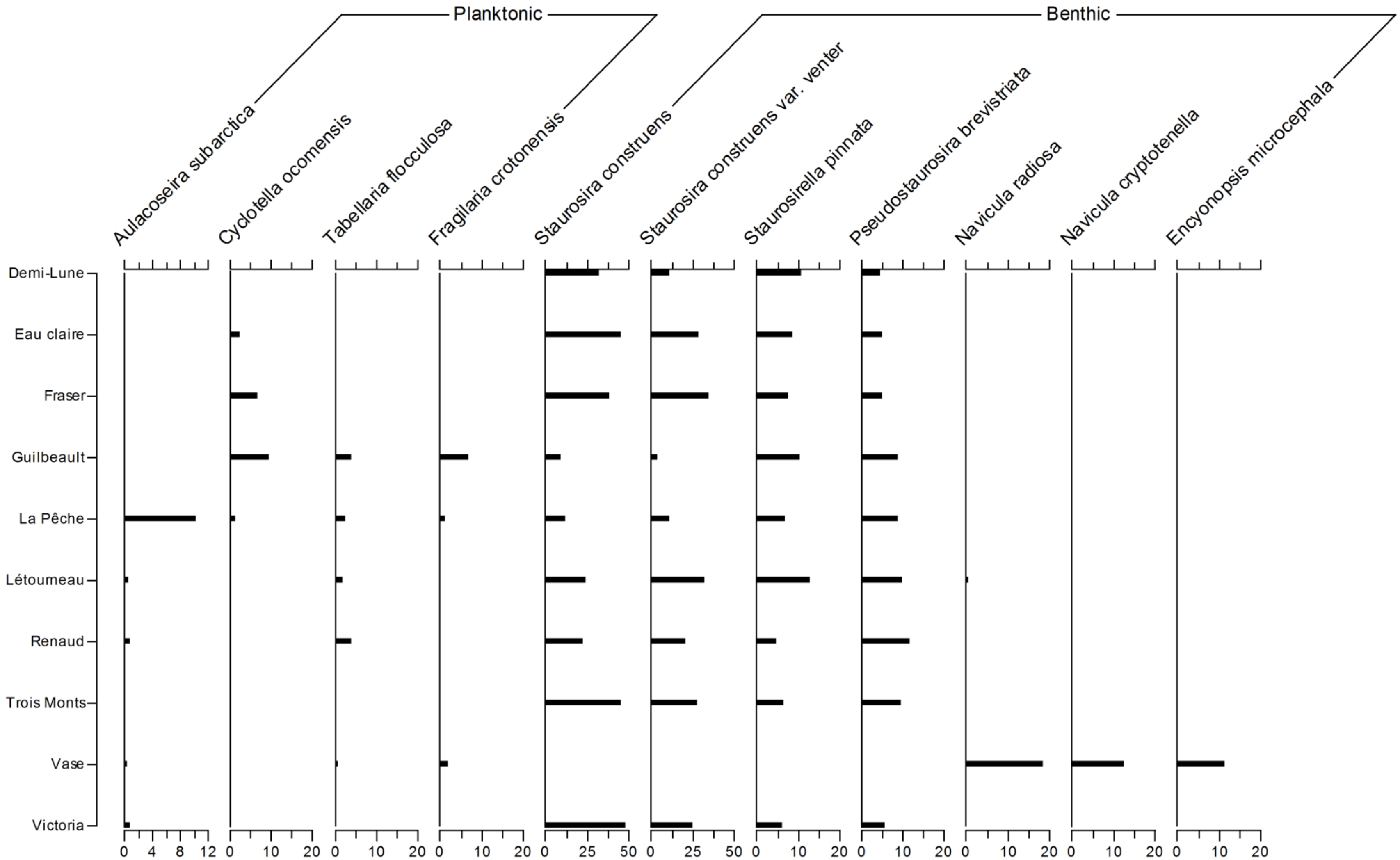

Figure 3.2 The relative abundance of dominant diatom taxa in surficial sediments of the 10 training set lakes dominated by benthic species. The three dominant taxa of each lake are represented.

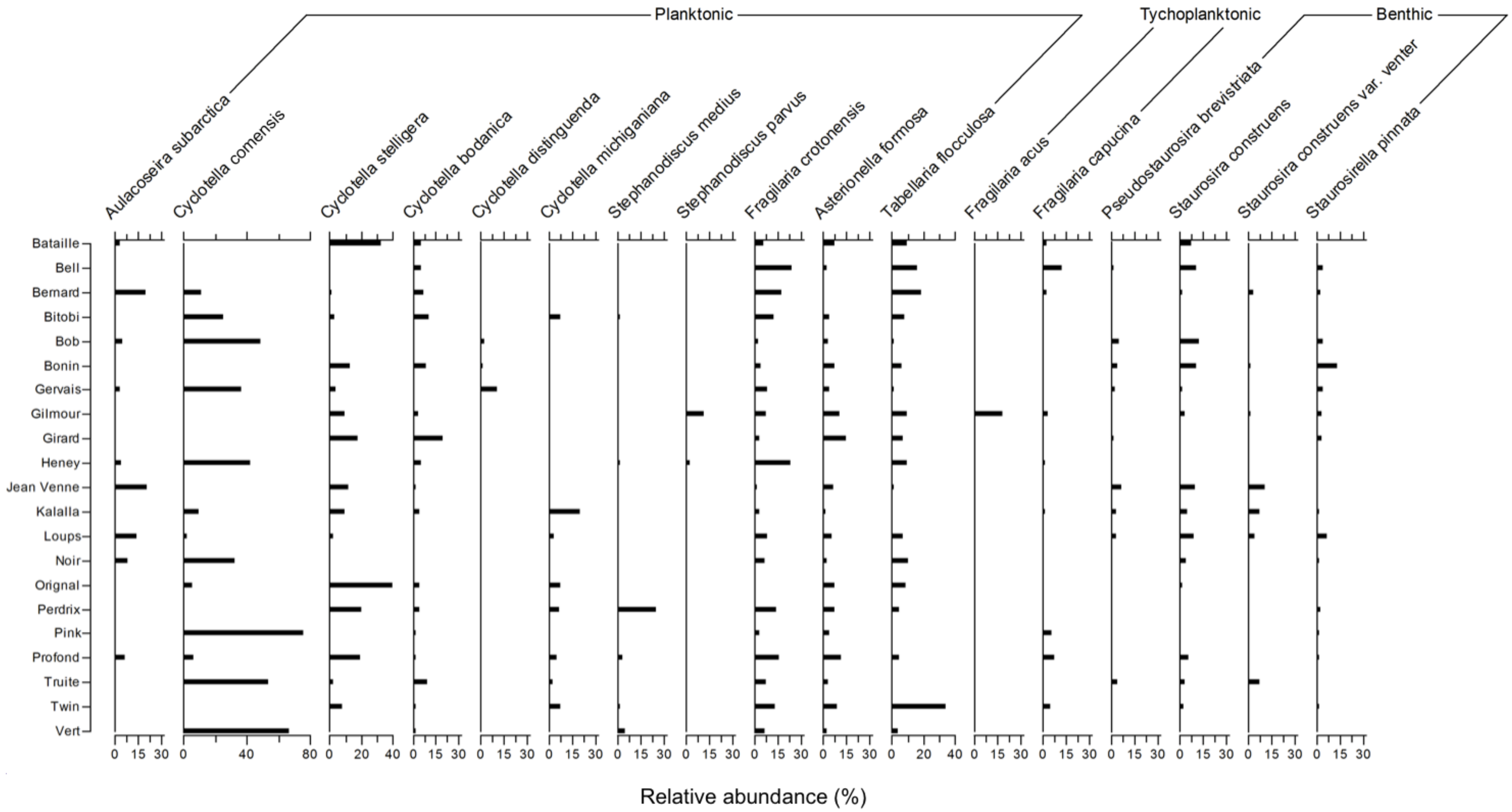

Figure 3.3 The relative abundance of dominant diatom taxa in surficial sediments of the 20 training set lakes dominated by planktonic species, along with lake Heney surficial sediments. The three dominant taxa of each lake are represented.

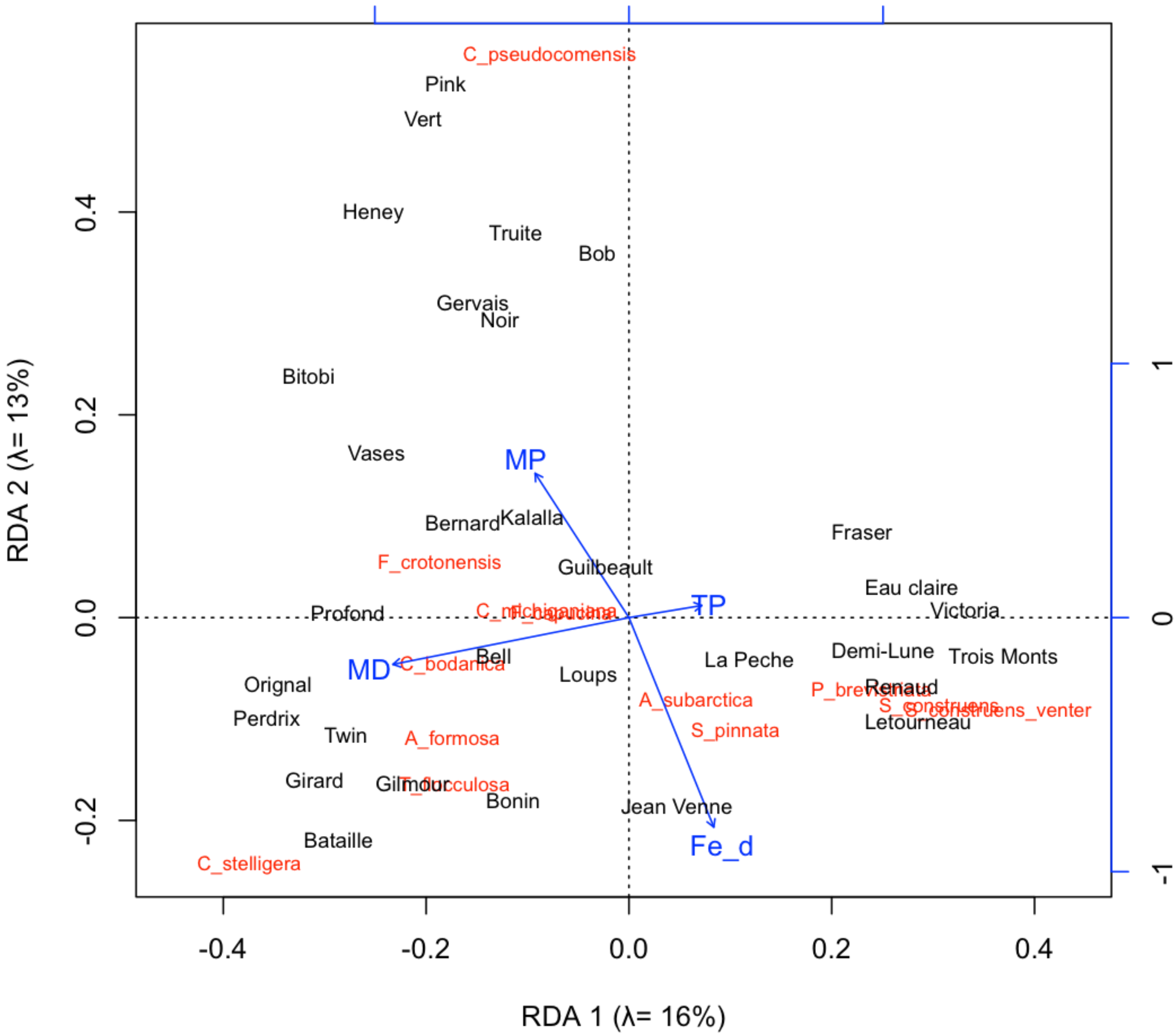

Figure 3.4 Redundancy analysis (RDA) plot showing diatom assemblage data and the 31 study lakes in relation to forward selected environmental variables. The variables percent marble (MP), max depth (MD), dissolved iron (Fe_d) were significant, but not total phosphorus (TP) (p-value = 0.14).

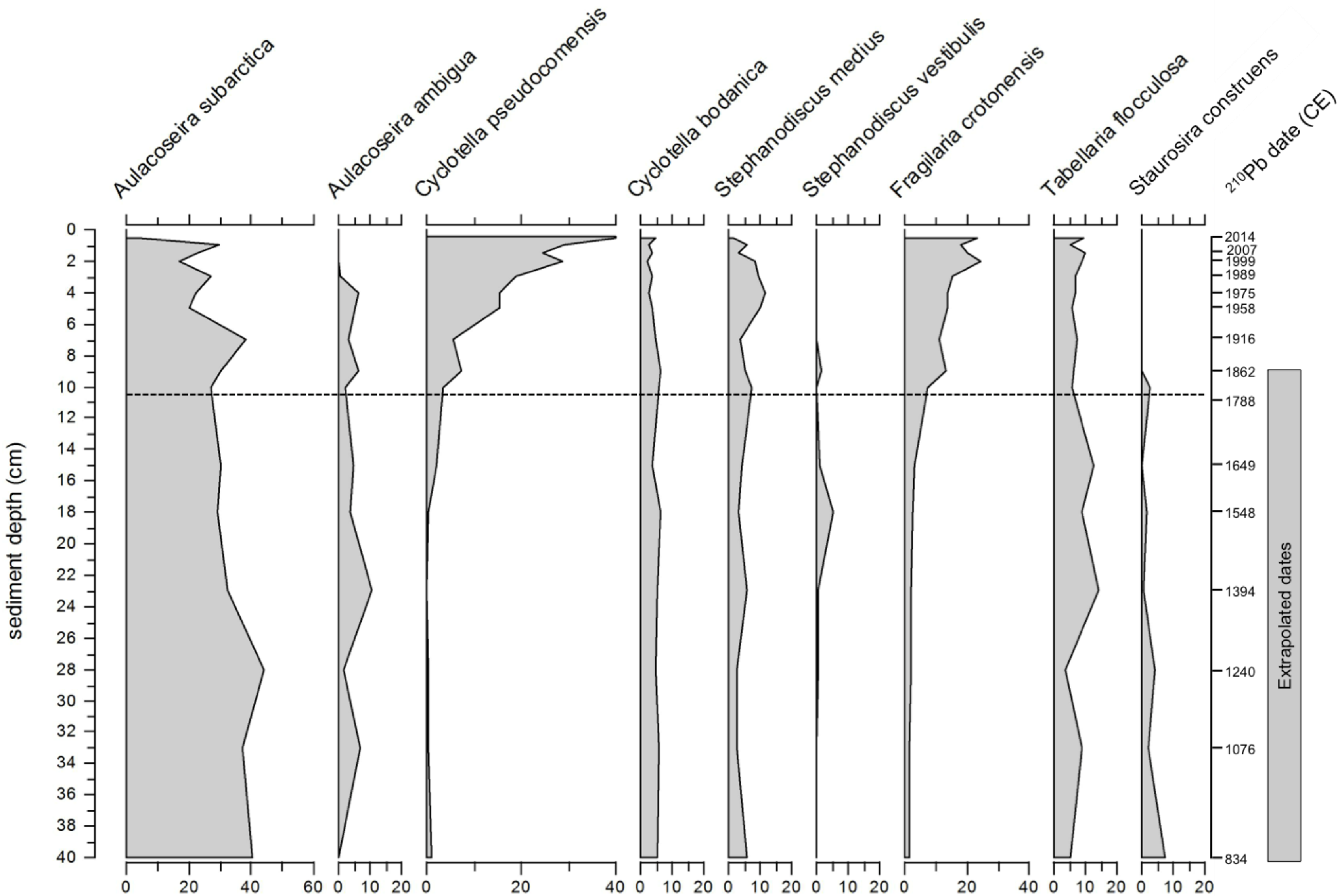

Figure 3.5 Stratigraphic plot of the relative abundance of dominant diatom taxa through Heney Lake sediment core, diatom-inferred total phosphorus (DI-TP) and ^{210}Pb year. CE, common era. Taxa are represented if they are present in >5% abundance in at least one subsample. The dashed line represents the approximate timing of European settlement.

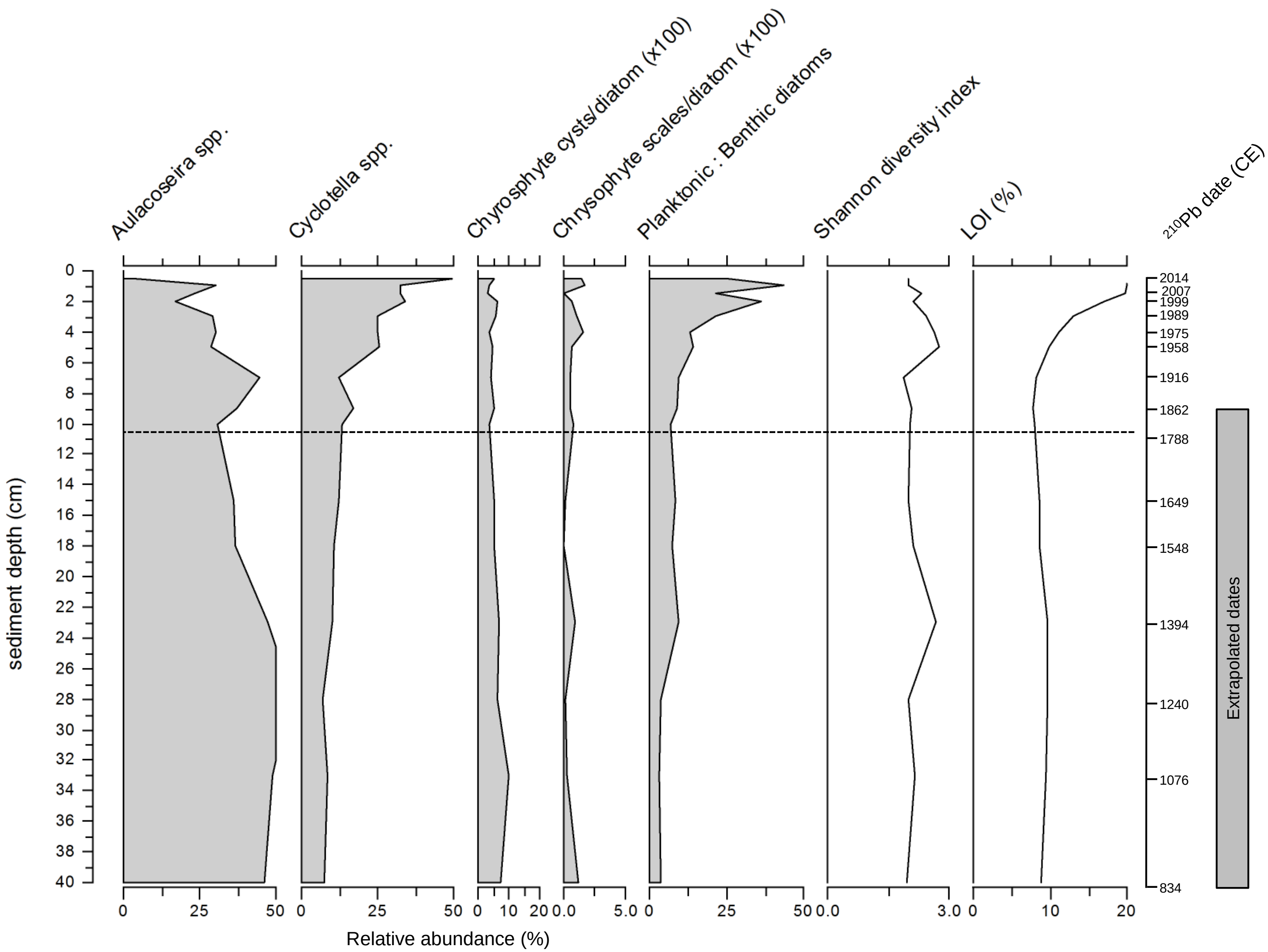

Figure 3.6 Stratigraphic plot of the relative abundance of the two dominant planktonic diatom genera through Heney Lake sediment core, along with the chrysophyte cysts and scales relative abundance, the planktonic: benthic diatom ratio, loss on ignition and ^{210}Pb year. CE, common era. The dashed line represents the approximate timing of European settlement.

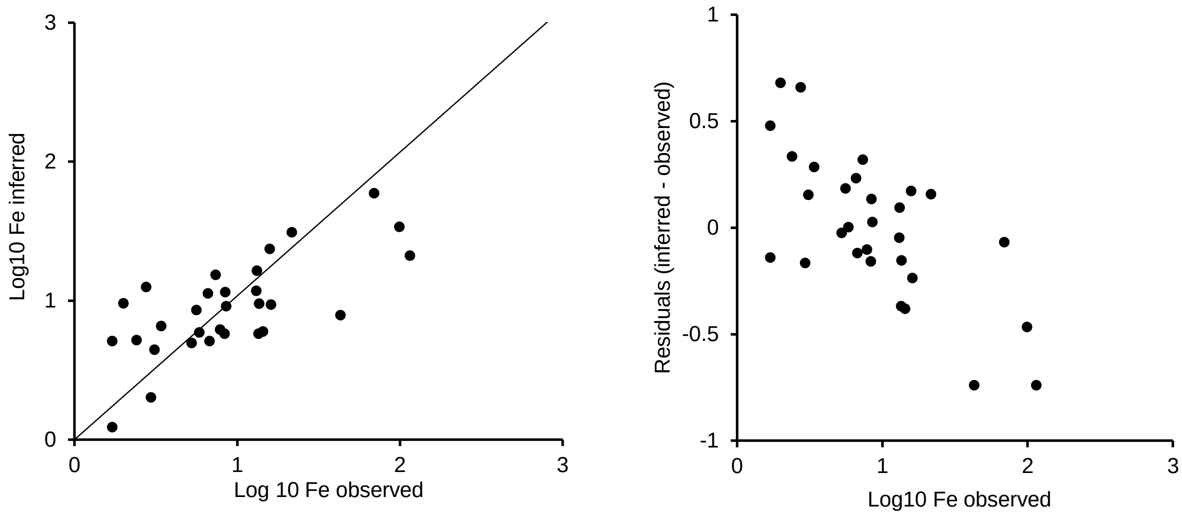

Figure 3.7 A) Dissolved iron (Fe_d) $\log_{10}$ observed against Fe_d $\log_{10}$ values inferred with the inverse shrinking averaging model (WA_Inv) ; B) residuals against predicted values.

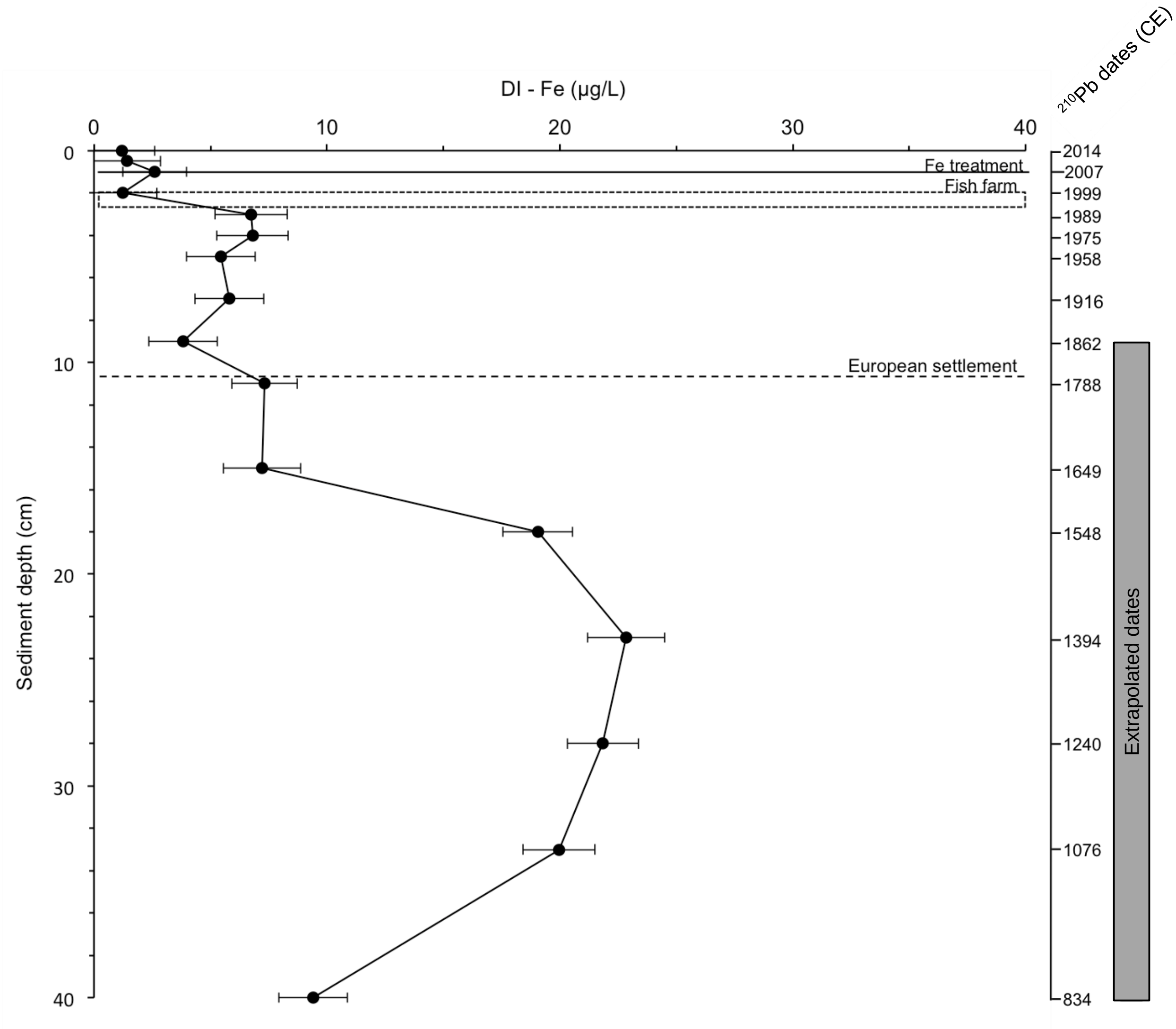

Figure 3.8 Sediment core depth profile of the diatom-inferred epilimnetic dissolved iron concentrations in Heney Lake, Québec. The dashed line represents the approximate timing of European settlement, the dotted box represents the approximate period of the fish farming activities (1993 – 1999) while the solid line represents the timing of the iron treatment (2007).

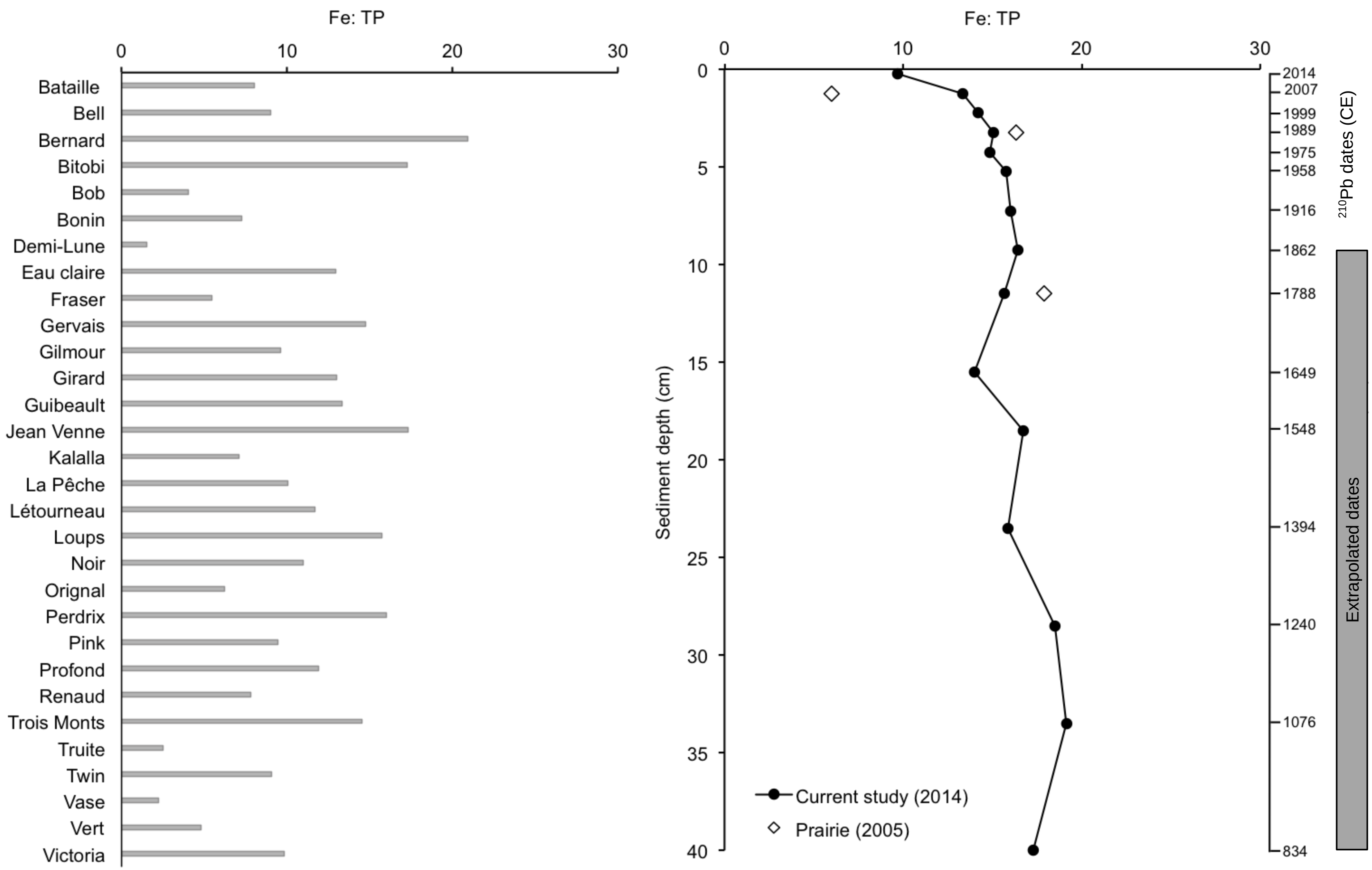

Figure 3.9 Iron to phosphorus ratio in the training set lakes (left panel), as well as in Heney Lake sediment core (right panel). Results from Prairie (2005) on a sediment core from Heney Lake are also shown in the right panel.

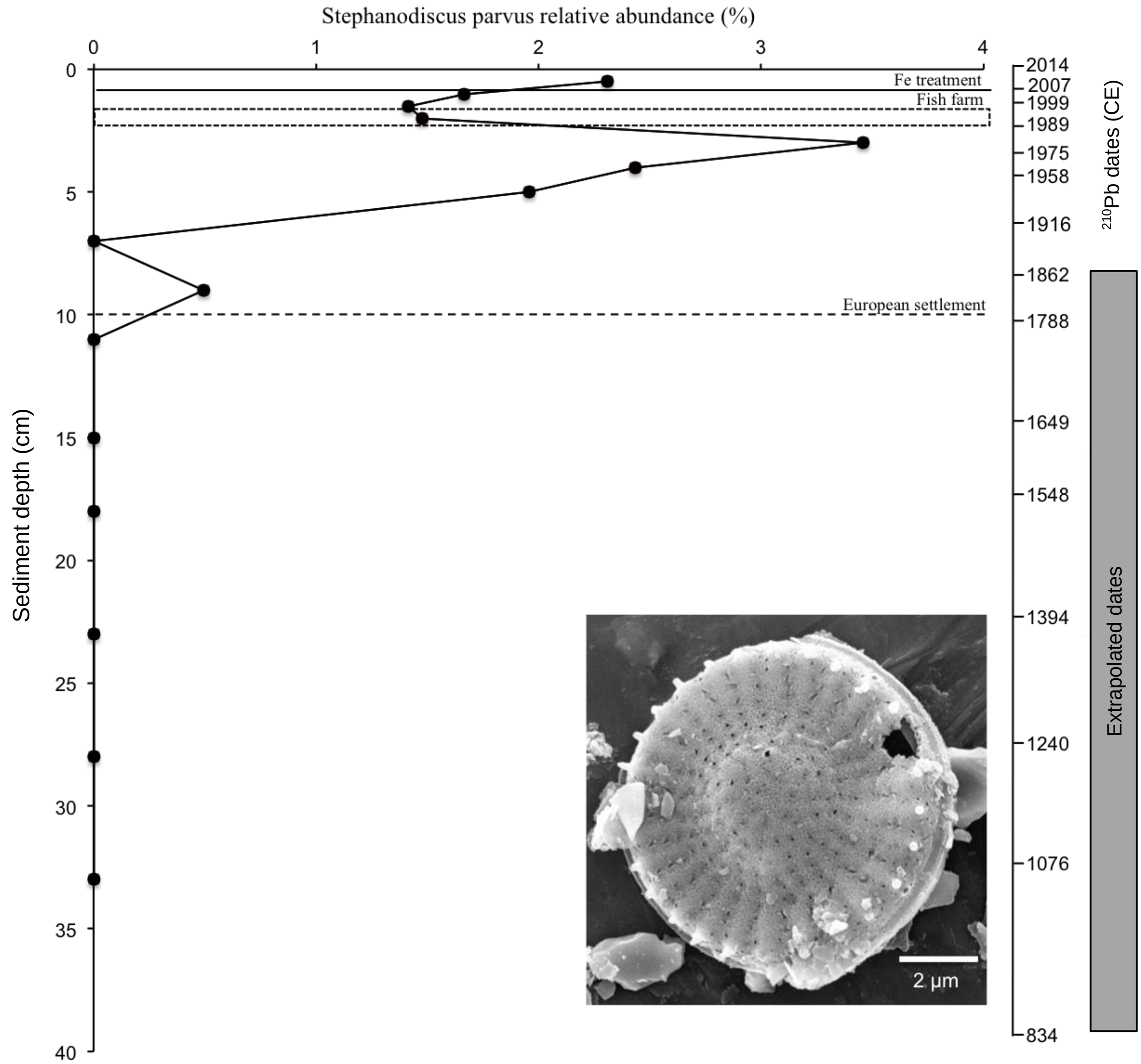

Figure 3.10 Changes in the abundance of *Stephanodiscus parvus* from the paleolimnological record of Heney Lake, Québec. The dashed line represents the approximate timing of European settlement, the dotted box represents the approximate period of the fish farming activities (1993 – 1999) while the solid line represents the timing of the iron treatment (2007).

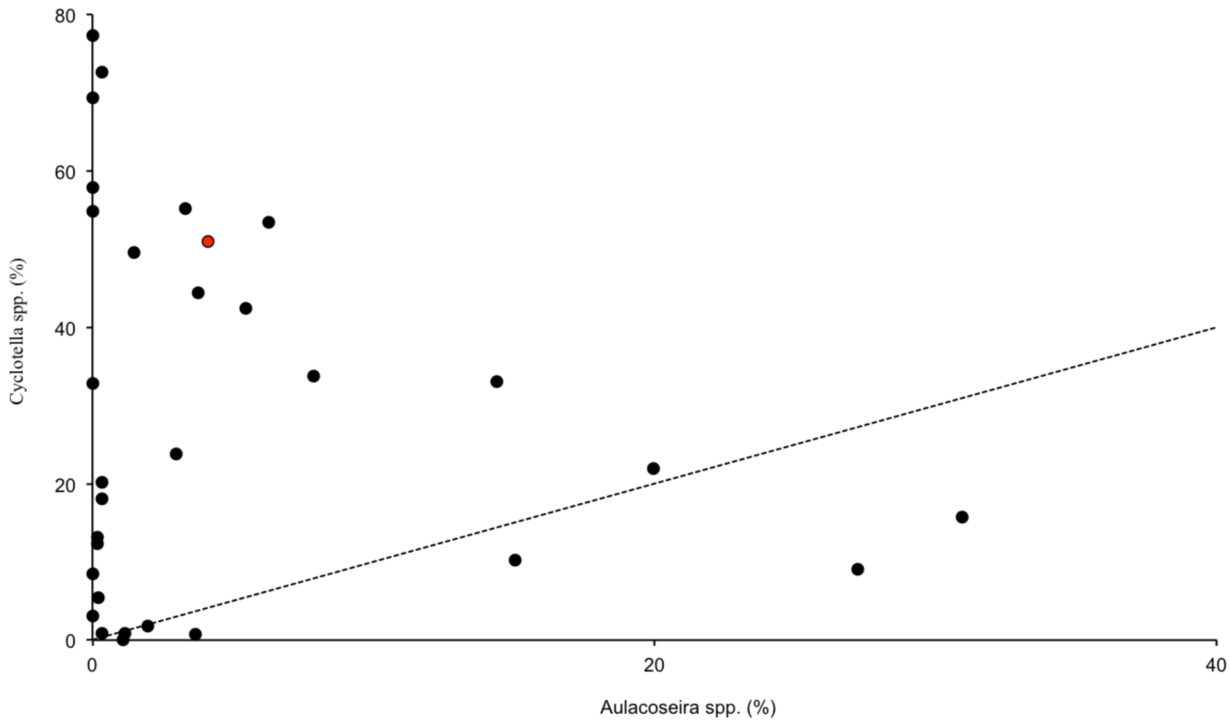

Figure 3.11 Relative abundance of *Cyclotella* spp. vs *Aulacoseira* spp. in the surficial sediments of the study lakes. The red symbol indicates Heney Lake and the dotted line represnts a 1:1 ratio.

4. General conclusions

I hypothesized that lakes of the Precambrian Shield with more marble in their catchment may be more susceptible to eutrophication, as this carbonate rock contains little iron concentrations and that the latter is a key element for the in-lake P dynamics. In order to test this hypothesis, I sampled over 30 lakes of the Outaouais region, southwestern Québec, and established their water and surficial sediment chemistry, as well as their catchment bedrock geology.

Additionally, I had hypothesized that a paleolimnological approach would allow for the reconstruction of trophic conditions of one Precambrian Shield lake, Heney Lake, which had undergone cultural eutrophication in the past century. Using fossil diatoms, a common paleolimnological indicator, I built a transfer function based on 30 training set lakes of the Outaouais and I was able to detect some effects of human activities on Heney Lake since European settlement. These activities included forest clear-cutting, housing development and more importantly, a fish farm and a subsequent iron treatment.

First, our results showed that the percent marble in the catchment did have some significant impact on the lake water chemistry. The calcium concentration, as well as alkalinity, was significantly higher in lakes with a large proportion of marble in their watershed. The percent marble also had some indirect, yet detectable, effect on the iron-phosphorus dynamics. Lakes with more marble in their catchment, and hence higher calcium concentrations, had lower Fe: TP ratios in surface waters and in the seston, as indicated by the models established by the stepwise regression analyses.

These results provided some evidence that lakes with a higher proportion of marble in their catchment were more vulnerable to iron deficiency, as Carignan (2003) suggested for Heney Lake. However, we obtained no evidence that Fe-deficient lakes were more vulnerable to eutrophication as neither the water, seston nor sediment Fe: TP ratios explained a significant proportion of the variation in the lake TP, TKN and chlorophyll *a*. Importantly though, the vast majority of our study lakes had a Fe: TP ratio below the threshold suggested by Jensen et al. (1992), below which internal loading is likely to occur if anoxic conditions develop. Anticipated effects of climate change include the extension of the growth season, allowing in-lake productivity increases and oxygen depletion in the hypolimnion. These conditions will likely induce internal loading in those lakes with low Fe, as the majority of our study lakes. Internal loading may lead to cyanobacterial blooms, as already observed in two of our study lakes, Lac La Pêche and Lac des Loups, during the fall season in the past decade (Leblanc et al., 2008).

The establishment of the study lake water chemistry then allowed the reconstruction of some paleolimnological conditions of Heney Lake using diatoms as paleoindicators. The RDA revealed that TP was not a statistically significant driver of the diatom community composition among lakes of this training set, as opposed to findings of a majority of paleolimnological studies (e.g. Smol, 2008; Smol, 2010; Hadley et al., 2013; Tremblay et al., 2014), and so no reliable reconstruction of this variable could be performed. Interestingly though, dissolved iron was a significant driver of the diatom community and therefore, a paleolimnological reconstruction of this variable was carried. To our knowledge, no previous studies have attempted to reconstruct past iron concentrations using diatoms, but a few studies have found some significant relationships between iron and diatom community structure (Larson et al., 2015; Tremblay et al., 2014).

The fish farm in Heney Lake from 1993 to 1999 was largely blamed for the water quality deterioration and lead to an important environmental class action lawsuit. Despite our unability to perform a TP reconstruction of Heney Lake, the diatom species *Stephanodiscus parvus* and *Fragilaria crotonensis*, typically associated with eutrophication conditions (e.g. Berthon et al., 2014; Heinsalu et al., 2007), were identified in the Heney Lake sediment core. Changes in these species relative abundances throughout the core indicated that Heney Lake exhibited signs of eutrophication well before the beginning of the fish farm activities, beginning in the early XXth century. Also, the diatom-inferred Fe concentrations decreased within the same time period while the organic content (LOI) gradually rose. These results suggest that Heney Lake's water quality degradation was probably more importantly linked to the logging industry and the housing development in the vicinity. The fish farm seemed to reduce the amount of Fe in the water column, probably because the P added through feed and fish faeces bounded to Fe and sank to the surface sediments. Additionally, a shift from *Aulacoseira* spp. to *Cyclotella* spp. (mainly

C. comensis) was observed in the sediment, beginning ca. 1960, which was likely due to some climate change effect such as the increased strength and duration of summer stratification.

In order to improve our model's ability to predict in-lake water chemistry based on basin characteristics, a first improvement would be to increase the sample size, and selecting more isolated lakes to balance the number of drainage vs. isolated lakes. Also, one approach might be to include more detailed geographical analyses of the land use and land cover, as well as the percent of wetland and other water bodies in each lake's catchment. Between 17 and 39% of the variation in lake water chemistry variables was explained by our models based only on basin characteristics. Perhaps including a slope catchment index would also improve the models, as d'Arcy & Carignan (1997) found. As for the paleolimnological reconstruction of Heney Lake, a larger spectrum of TP conditions in the training set lakes would be required to reconstruct this variable. However, it appears that the Outaouais region has few meso- to eutrophic lakes, so expanding the research area to other similar regions on the Shield would probably be necessary. As we found no other study that inferred Fe using diatoms, future research should focus on the effect of this micronutrient on the diatom communities and assess the validity of diatom-based Fe reconstruction by comparing inferred values with long-term monitoring data where possible.

Using surface water chemistry, geographical tools, surficial sediments and a sediment core from Heney Lake, we were able to determine relationships between catchment physical properties and lake water chemistry and demonstrate that lakes with more marble in their watershed were more prone to iron deficiency. We were also able to reconstruct some paleolimnological conditions and found evidence that Heney Lake showed signs of eutrophication before the beginning of the fish farm, likely associated with the forest clearing and housing development. Interestingly, the most significant change to Heney Lake in the past 200 years may have resulted from climate change, as indicated by the clear shift in the fossil diatom community from *Aulacoseira* spp. to *Cyclotella* spp., a trend also observed in a large number of lakes throughout North America and Europe (Rühland et al., 2008). This common and widespread shift provides a portrait that climate-driven, species-specific changes are now obvious across a wide spectrum of lakes, and may serve as a distinctive biostratigraphic indicator of the Holocene-Anthropocene transition.

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Appendix I Main Physical and chemical characteristics of the 31 lakes sampled in the Western Québec. Numbers in bold indicate a random number was generated between 0 and the detection limit because one or more replicates had a value below the detection limit.

Lake	#	Lat. (º)	Long. (º)	Elev. (masl)	Surface area (hectares)	Catchment area (hectares)	Catchment area: Surface area	Max depth (m)	House density (# houses/km shoreline)	Percent marble in catchment (%)	TP (µg/L)	TKN (µg/L)	TKN:TP (weight)	Fe dissolved (µg/L)	Fe: TP water
Bataille	1	45.67153	75.5683	237	58.06	132.23	2.28	53	10.88	0.00	**4**	230	57.50	4.60	1.15
Bell	2	45.64888	75.96854	150	11.48	164.51	14.33	19	16.17	7.10	9	355	39.44	2.40	0.27
Bernard	3	45.75839	75.97549	171	484.03	5605.57	11.58	24	8.94	36.37	6.5	305	46.92	13.40	2.06
Bitobi	4	46.10477	75.94510	141	189.44	2851.91	15.05	19.2	4.72	72.44	5	305	61.00	12.50	2.5
Bob	5	45.67700	76.29401	204	19.80	1198.00	60.52	10	4.65	78.63	6	245	40.83	4.85	0.81
Bonin	6	45.67196	75.69820	176	31.88	711.23	22.31	40	5.42	0.30	**3**	245	81.67	7.45	2.48
Demi-Lune	7	45.74100	75.98710	192	4.43	14.43	3.26	13	4.33	43.32	**7**	435	62.14	5.60	0.80
Eau Claire	8	45.66591	75.61942	168	11.43	95.17	8.33	20	7.41	3.26	8.5	265	31.18	1.75	0.21
Fraser	9	45.65048	75.97519	153	7.45	33.74	4.53	7	14.88	8.62	6	345	57.50	1.00	0.17
Gervais	10	45.64392	76.12200	164	10.69	127.76	11.96	15	10.84	55.15	6.5	285	43.85	7.35	1.13
Gilmour	11	45.63647	75.55085	136	29.34	90.15	3.07	40.7	9.82	26.50	5	265	53.00	7.55	1.51
Girard	12	45.64779	75.75067	179	32.70	199.94	6.11	25	6.54	5.11	4	240	60.00	12.1	2.42
Guibeault	13	45.73732	76.26270	236	5.76	1046.32	181.75	8.5	7.56	15.51	11	375	34.09	12.6	1.15
Heney	14	46.02245	75.92872	144	1231.14	7867.47	6.39	34	8.80	50.13	10.5	345	32.86	2.05	0.20
Jean Venne	15	45.67933	76.05975	206	15.27	122.69	8.04	7.5	8.07	0.00	8	295	36.88	98.25	12.28
Kalalla	16	45.73527	75.98163	199	3.07	23.18	7.56	9	2.72	67.65	**2.5**	360	144.00	15.15	6.06
La Pêche	17	45.6185	76.18400	181	685.65	3758.20	5.48	10	0.19	2.62	**2**	265	132.50	6.35	3.18
Letourneau	18	45.5969	75.66857	128	23.13	3720.49	160.82	4.4	9.62	6.87	9.5	385	40.53	114.25	12.03
Loups	19	45.6822	76.19790	195	109.03	6661.90	61.1	8.5	16.45	26.57	7.5	325	43.33	12.20	1.63
Noir	20	46.00774	75.94870	145	56.33	300.31	5.33	7.2	1.68	4.22	22.5	570	25.33	2.10	0.09
Orignal	21	46.10669	76.08024	170	51.61	250.83	4.86	27.2	5.84	100.00	7.5	415	55.33	4.25	0.57
Perdrix	22	45.59250	75.68441	156	45.27	371.25	8.2	27.1	9.30	35.97	6.5	270	41.54	6.85	1.05
Pink	23	45.46830	75.80700	164	11.74	83.62	7.13	18	0.00	0.00	**2**	195	97.50	1.95	0.98
Profond	24	46.15319	76.10100	175	90.55	473.06	5.22	33.8	4.08	63.33	**2.5**	190	76.00	1.40	0.56
Renaud	25	45.60260	76.02320	203	10.46	1078.78	103.17	5	0.72	0.00	9	340	37.78	68.30	7.59
Trois Monts	26	45.73158	76.23718	224	11.19	1931.85	172.63	1.2	1.62	22.64	9.5	395	41.58	20.65	2.17
Truite	27	46.16553	76.08949	184	14.45	44.15	3.06	17	0.50	100.00	5.5	235	42.73	0.70	0.13
Twin	28	45.60707	75.54813	124	56.46	2187.01	38.74	23	12.37	19.98	8	310	38.75	42.05	5.26
Vases	29	46.12979	76.12836	176	58.01	5962.09	102.77	1	0.80	39.63	9	475	52.78	5.75	0.64
Vert	30	46.00139	75.94083	144	129.95	598.86	4.61	13.2	4.04	47.70	7	410	58.57	0.70	0.10
Victoria	31	46.07885	75.95776	149	136.90	954.49	6.97	6.8	2.11	60.13	6	375	62.50	14.8	2.47

APPENDIX I (continued)

Lake	Chl a (µg/L)	TP particulate (µg/L)	Fe particulate (µg/L)	Fe: TP particulate	pH	DO (mg/L)	Conductivity (µS/cm)	Ca (mg/L)	Secchi (m)	Alkalinity (m eq/L)	TP in surface sediments (mg/kg)	Fe in surface sediments (mg/kg)	Fe: TP ratio in surface sediments	Sediment LOI_{550} (%)	Sediment LOI_{950} (%)
Bataille	0.96	2.03	25.06	12.37	7.97	9.01	95	14.10	8.08	39,0	1.70	13.66	8.02	46.53	49.9
Bell	3.03	4.54	10.534	2.32	8.05	9.63	231.4	20.40	2.9	74,0	1.82	16.34	8.98	38,00	42.03
Bernard	2.09	4.73	24.98	5.28	8.4	9.51	147.9	23.55	4.4	69.635	1.56	32.76	20.94	36.11	39.73
Bitobi	1.90	3.16	21.35	6.75	8.44	10.25	96	13.60	4.52	69.38	1.64	28.34	17.23	7.75	8.74
Bob	0.59	3.61	8.02	2.22	8.12	9.35	231.2	36.10	5.91	104,0	3.12	12.62	4.05	51.15	54.24
Bonin	4.28	2.23	9.87	4.43	7.92	9.04	67.7	11.15	5.23	27.75	2.06	13.98	6.79	40.74	50.03
Demi-Lune	2.37	1.99	10.20	5.12	8.74	9.62	205.1	37.50	6	109.17	5.28	8.03	1.53	69.11	71.48
Eau Claire	0.99	3.48	4.58	1.32	8	9.52	95.3	15.25	6.99	38.75	1.26	16.31	12.96	39.31	43.28
Fraser	2.17	3.81	11.15	2.93	8.27	9.43	218.4	31.65	3.6	90.75	1.68	9.17	5.45	59.69	62.47
Gervais	3.47	3.83	40.78	10.65	7.84	8.64	103	14.80	3.08	42.75	1.58	23.31	14.72	30.46	34.10
Gilmour	1.10	2.40	14.09	5.86	8.16	9.8	102.8	11.60	7.92	88.3	1.49	14.38	9.63	34.39	38.54
Girard	0.97	2.12	11.67	5.50	8.04	9.28	80.8	12.45	4.18	32,0	2.71	35.22	13.01	39.74	44.11
Guibeault	4.49	6.51	73.97	11.36	7.25	6.56	147.1	25.65	2.34	67.5	1.65	22.06	13.35	56.96	61.41
Heney	3.80	6.45	13.29	2.06	8.62	10.1	131.5	19.4	2.47	88.3	2.63	25.48	9.70	20.44	22.76
Jean Venne	2.82	3.09	29.47	9.54	7.36	8.34	43.7	5.70	2.54	15.25	3.07	53.10	17.28	40.11	43.60
Kalalla	1.09	2.93	15.09	5.15	8.62	9.22	234.5	38.05	3	116.67	2.64	18.75	7.10	60.10	64.51
La Pêche	1.73	6.97	103.80	14.88	7.86	8.21	101.4	14.85	4.8	40.75	1.50	15.05	10.03	48.45	51.04
Letourneau	3.99	5.57	32.16	5.77	8.32	10.17	112.9	16.20	1.96	122.975	1.73	20.17	11.67	24.16	26.38
Loups	2.67	15.74	22.20	1.41	8.11	8.47	161.1	23.45	2.9	64.5	1.61	25.24	15.72	32.39	35.40
Noir	7.62	2.68	15.92	5.93	8.13	9.6	159.8	25.65	2.35	107.2	1.67	18.30	10.98	24.76	26.16
Orignal	1.56	2.14	11.47	5.36	8.6	10.16	120	19.30	8.6	94.6	2.59	16.13	6.24	64.16	67.04
Perdrix	1.14	4.06	15.48	3.81	8.62	10.15	157.5	24.85	6.74	157.65	1.35	21.61	15.99	31.23	35.35
Pink	0.31	2.27	7.47	3.30	8.15	7.55	242.8	40.80	5.25	103.75	1.22	11.32	9.31	50.49	53.57
Profond	0.56	2.32	13.43	5.80	8	11.62	82.4	11.65	7.96	56.75	1.66	19.76	11.89	36.95	39.63
Renaud	2.36	3.77	29.77	7.89	6.75	6.28	70	10.25	1.7	29.75	1.77	13.82	7.80	50.83	53.99
Trois Monts	4.13	6.76	104.81	15.50	7.6	8.72	153.8	25.00	1.2	68,0	1.52	21.63	14.23	68.40	70.44
Truite	1.31	7.34	11.09	1.51	8.6	11.16	226.9	33.20	5.72	170.3	3.14	7.91	2.52	46.67	49.83
Twin	2.56	3.84	39.66	10.33	7.79	9.02	110.6	17.45	3.3	44.33	2.00	18.03	9.04	19.52	23.00
Vases	2.17	5.35	21.21	3.97	8.51	11.46	129.1	18.95	1.2	94.6	0.72	1.59	2.22	83.60	86.59
Vert	3.19	4.58	12.57	2.74	8.63	10.06	158.8	26.10	3.66	107.2	2.85	13.59	4.78	46.35	49.49
Victoria	1.38	4.26	20.75	4.87	7.96	9.11	131.7	19.80	4.32	94.6	2.17	21.18	9.78	32.69	34.42

APPENDIX II Pearson's coefficients for water quality variables and lake and catchment morphometric variables. Only significant coefficients are shown. * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$. Numbers in bold are significant based on Bonferroni-adjusted probabilities.

	El	SA	CA	CA_SA	MD	HD	MP	TP	TKN	Fe_d	Fe_TP_w	Chl	TP_p	Fe_p
El	-													
SA	-0.53**	-												
CA		**0.69*** **	-											
CA_SA			**-0.62*** **	-										
MD				0.54**	-									
HD					0.36*	-								
MP							-							
TP					-0.37*			-						
TKN					-0.58***			**0.72*** **	-					
Fe_d				-0.56**						-				
Fe_TP_w				-0.42**						**0.92*** **	-			
Chl								**0.68*** **	**0.70*** **			-		
TP_p				-0.36*	-0.49**			**0.77*** **	0.58***			0.60***	-	
Fe_p			0.43*	-0.53**	-0.41*			0.42*	0.38*	**0.66*** **	0.48**	0.55**	0.44*	-
Fe_TP_p										**0.74*** **	**0.75*** **			**0.77*** **
pH				0.42*			0.58***			-0.49**	-0.44*			-0.39*
Cond							0.38*			-0.47**	-0.48**			
Cal							0.38*			-0.44*	-0.44*			
Alk							0.54**			-0.36*	-0.39*		0.38*	
TP_s			-0.36*											
Fe_s						0.36*				0.47**	0.43*			
Fe_TP_s										0.40*	0.37*			0.39*
LOI	0.49**	-0.45*			-0.39*	-0.38*								

APPENDIX II (continued)

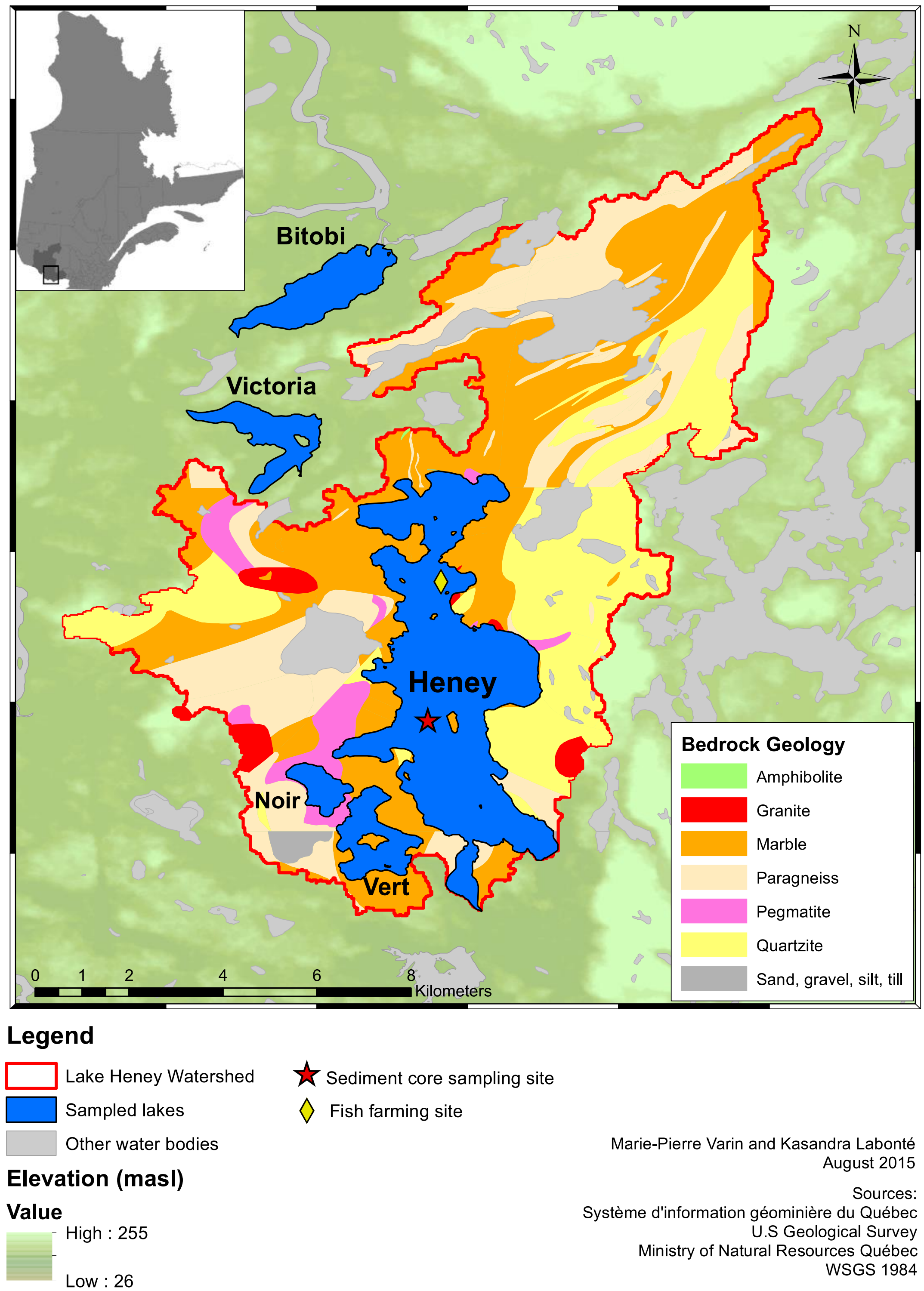
	Fe_TP_p	pH	Cond	Cal	Alk	TP_s	Fe_s	Fe_TP_s
El								
SA								
CA								
CA_SA								
MD								
HD								
MP								
TP								
TKN								
Fe_d								
Fe_TP_w								
Chl								
TP_p								
Fe_p								
Fe_TP_p	-							
pH	-0.44*	-						
Cond	-0.43*	0.51**	-					
Cal	-0.39*	0.51**	**0.96*** **	-				
Alk	-0.40*	**0.69*** **	**0.73*** **	**0.71*** **	-			
TP_s						-		
Fe_s				-0.45*	-0.40*		-	
Fe_TP_s				-0.40*	-0.39*		**0.83*** **	-
LOI							-0.56**	-0.58***

APPENDIX III Multiple linear regression models

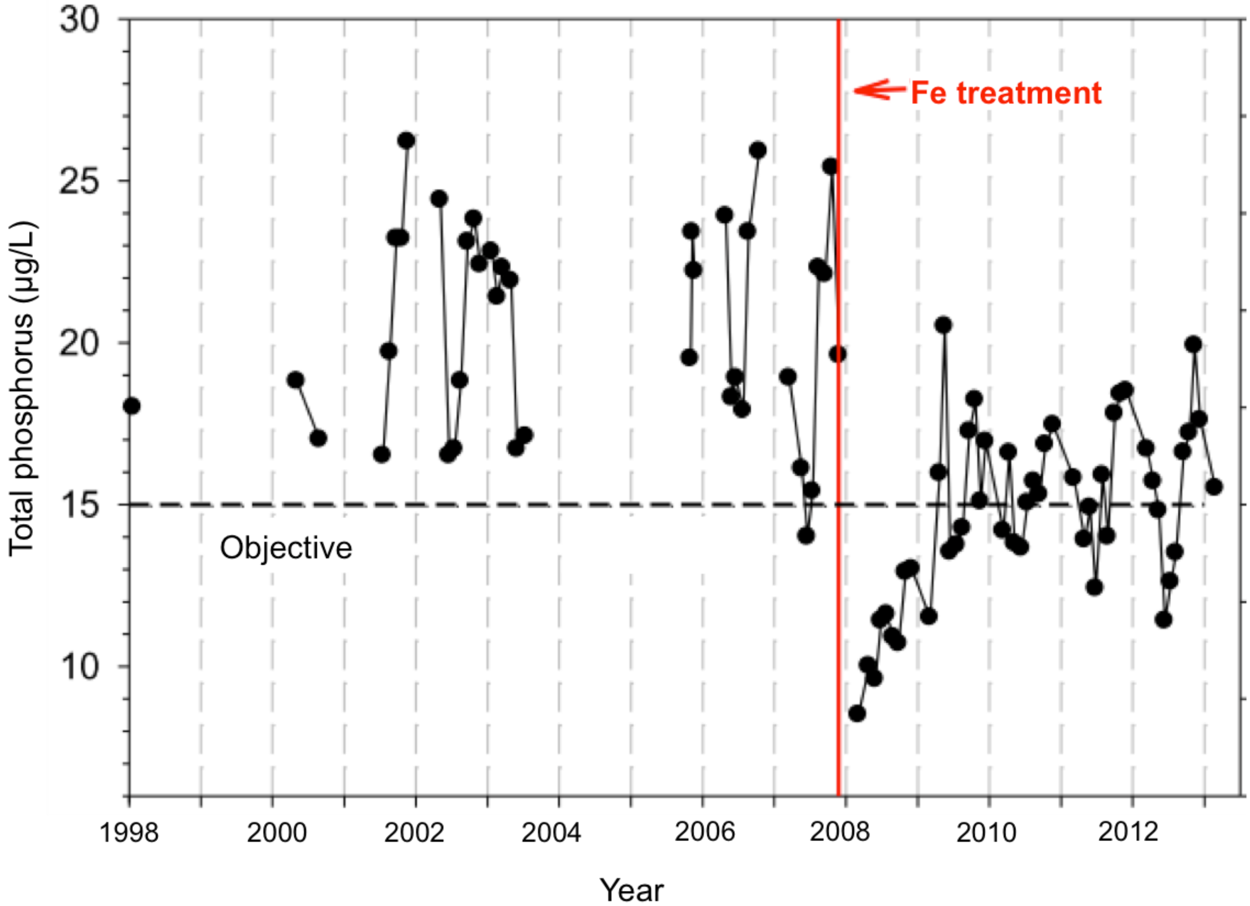
Range (unit)	Independent variable	Coeffitcient	SE	p-value	partial r^2_{adj}	Model r^2_{adj}	Model p-value
Model 1: Log(Calcium) based on basin characteristics							
5.7 - 40.8	Intercept	1.17	0.06	< 0.001		0.12	< 0.05
(mg/L)	sqrt(MP)	0.03	0.01	< 0.05			
Model 2: pH^2 based on basin characteristics							
6.75 - 8.74	Intercept	54.71	2.54	< 0.001		0.44	< 0.001
	sqrt(MP)	1.25	0.31	< 0.001	0.31		
	1/sqrt(CA_SA)	16.21	5.95	< 0.05	0.13		
Model 3: Log(TP) based on basin characteristics							
2 - 22.5	Intercept	0.87	0.11	< 0.001		0.25	< 0.01
(µg/L)	sqrt(MD)	-0.08	0.03	< 0.01	0.11		
	sqrt(HD)	0.1	0.04	< 0.05	0.14		
Model 3 *a*: Log (TP) based on all variables							
2 - 22.5	Intercept	-3.15	0.64	< 0.001		0.56	< 0.001
(µg/L)	Log(TKN)	1.52	0.25	< 0.001	0.49		
	Sqrt(HD)	0.06	0.03	< 0.05	0.07		
Model 4: Log(Fe_d) based on basin characteristics							
0.70 - 114.25	Intercept	1.46	0.20	< 0.001		0.29	< 0.01
	1/sqrt(CA_SA_	-1.94	0.54	< 0.01			
Model 5 *a*: Log (Fe: TP_{water}) based on basin characteristics							
0.09 - 12.28	Intercept	0.53	0.22	< 0.05		0.14	< 0.05
	1/sqrt(CA_SA)	-1.49	0.6	< 0.05			
Model 5 *b*: Log (Fe: TP_{water}) based on all variables							
0.09 - 12.28	Intercept	2.13	0.61	< 0.01		0.31	< 0.01
	Log(Cal)	-1.26	0.45	< 0.001	0.17		
	1/sqrt(CA_SA)	-1.41	0.54	< 0.05	0.14		
Model 6 *a*: Log (Fe: $TP_{particulate}$) based on basin characteristics							
1.32 - 15.5	NS						
Model 6 *b*: Log (Fe: $TP_{particulate}$) based on all variables							
1.32 - 15.5	Intercept	1.42	0.33	< 0.001		0.12	< 0.05
	Log(Cal)	-0.57	0.25	< 0.05			
Model 7 *a*: Sqrt (Fe: $TP_{sediments}$) based basin characteristics							
1.52 - 20.94	Intercept	1.48	0.58	< 0.05		0.18	< 0.05
	Log(CA)	0.35	0.17	< 0.05	0.09		
	Sqrt(HD)	0.28	0.13	< 0.05	0.09		
Model 7 *b*: Sqrt (Fe: $TP_{sediments}$) based on all variables							
1.52 - 20.94	Intercept	6.87	1.09	< 0.001		0.42	< 0.001
	LOI	-0.03	0.01	< 0.001	0.32		
	pH^2	-0.04	0.02	< 0.05	0.10		

Range (unit)	Independent variable	Coefficient	SE	p-value	partial r^2_{adj}	Model r^2_{adj}	Model p-value
Model 8 *a:* Log(Chl) based on basin characteristics							
0.31 - 7.62	Intercept	0.39	0.16	< 0.05		0.17	< 0.05
(µg/L)	Sqrt(MD)	-0.09	0.04	< 0.01	0.08		
	Sqrt(HD)	0.11	0.05	< 0.05	0.09		
Model 8 *b:* Log(Chl) based on all variables							
0.31 - 7.62	Intercept	-3.93	0.87	< 0.001		0.55	< 0.001
(µg/L)	Log(TKN)	2.11	0.34	< 0.001	0.48		
	Log(Cond)	-0.51	0.21	< 0.05	0.07		
Model 8 *c:* Log(Chl) based on all variables, using TP instead of TKN							
0.31 - 7.62	Intercept	-0.42	0.15			0.44	< 0.001
(µg/L)	Log(TP)	0.89	0.18	< 0.001			
Model 9: Alkalinity based on basin characteristics							
15.25 - 170.3	Intercept	47.62	10.7	< 0.001	0.26	0.26	< 0.01
(m eq/L)	Sqrt(MP)	6.45	1.88	< 0.001			
Model 10: Conductivity based on basin characteristics							
43.7 - 242.8	Intercept	2	0.06	< 0.001		0.12	< 0.05
(µS/cm)	Sqrt(MP)	0.02	0.01	< 0.05			
Model 11 *a:* Log(TKN) based on basin characteristics							
190 - 570	Intercept	2.66	0.04	< 0.001		0.31	< 0.001
(µg/L)	Sqrt(MD)	-0.04	0.01	< 0.001			
Model 11 *b:* Log(TKN) based on basin characteristics							
190 - 570	Intercept	2.09	0.12	< 0.001		0.68	< 0.001
(µg/L)	Log(TP)	0.28	0.05	< 0.001	0.5		
	Sqrt(MD)	-0.03	0.01	< 0.001	0.1		
	pH^2	0.01	0.001	< 0.01	0.08		

APPENDIX IV Lake Heney watershed bedrock composition.

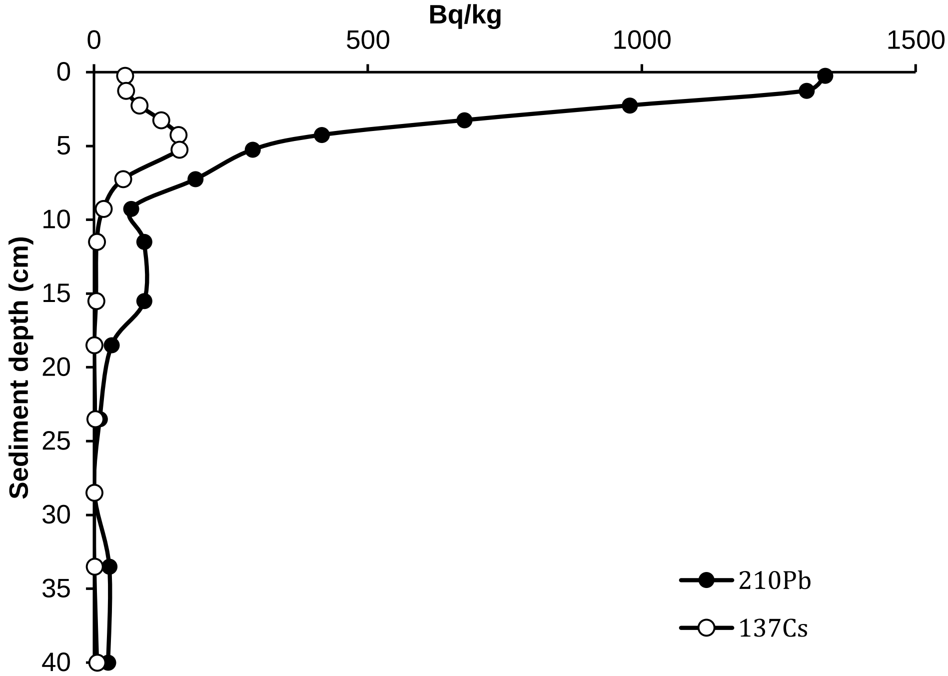


APPENDIX V Synthesis of TP concentrations in Heney Lake, averaged for the entire lake, measured by Carignan (2000-2013) and Prairie (2006). The red line represents the timing of the iron treatment and the black dotted line represents the TP objective of the Association for the Protection of Lake Heney.

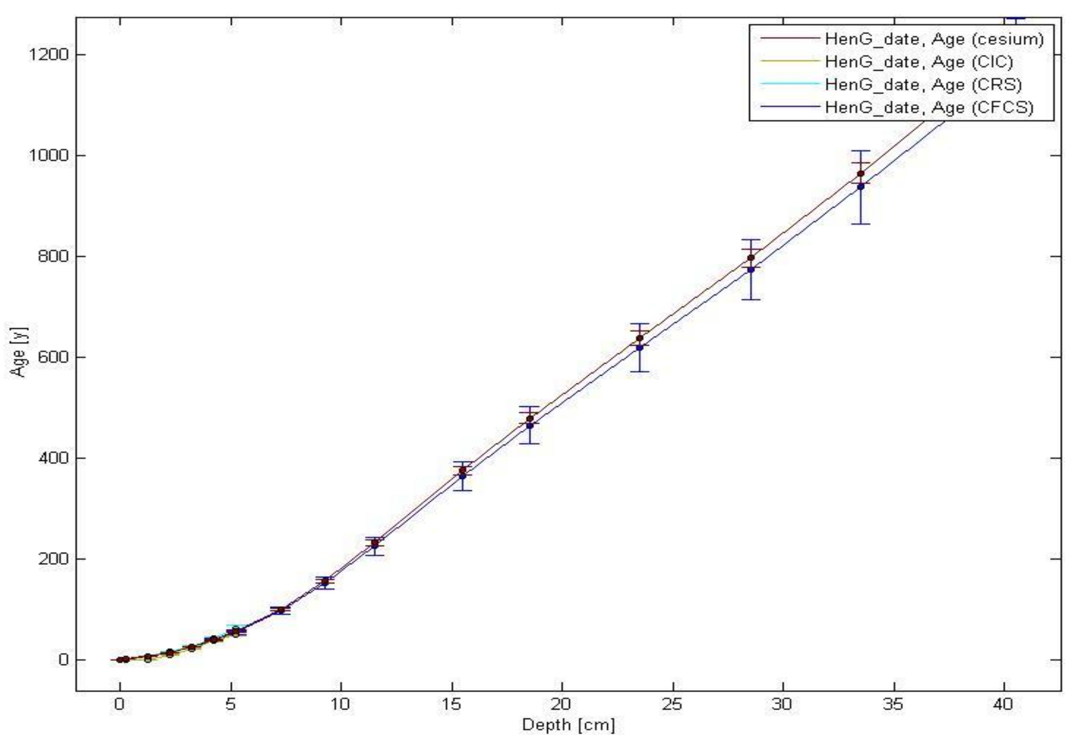


APPENDIX VI Radiometric dating analysis showing A) 210Pb and 137 Cs activity in becquerels per kilogram dry weight and B) comparison of the four dating models: 137cesium, Constant Initial Concentration (CIC), Constant Rate of Supply (CRS) and Constant Flux Constant Sedimentation Rate (CFCS) in Heney Lake sediment core.

A)



B)



APPENDIX VII A) Importance of each component retained in the principal component analysis; B) Loadings of each variable in the principal components retained in the principal component analysis and C) Scores of each lake on the principal components retained.

A)	PC1	PC2	PC3	PC4
Standard deviation	2.07	1.94	1.43	1.03
Proportion of variance	0.28	0.25	0.14	0.07
Cumulative proportion	0.28	0.53	0.67	0.74

B)	PC1	PC2	PC3	PC4
El	0.124		0.408	0.417
CA_SA	-0.319	0.150		0.481
MD	-0.224	0.360	-0.213	0.214
HD		0.117	-0.450	0.150
MP	-0.240	-0.193	-0.143	-0.264
TP	0.226	-0.273	-0.329	0.285
TKN	0.169	-0.395	-0.197	0.233
Fe_d	0.352			-0.319
Chl	0.298	-0.204	-0.332	0.241
pH	-0.358	-0.171	-0.222	
Cond	-0.274	-0.354		
Cal	-0.268	-0.363		
Alk	-0.290	-0.325		-0.111
Sec	-0.349	0.283		0.126
LOI		-0.210	0.491	0.349

C)

Lake	PC1	PC2	PC3	PC4
Bataille	-0.969	3.538	0.94	2.643
Bell	0.234	-0.71	-1.615	0.46
Bernard	-0.367	0.064	-0.811	-0.242
Bitobi	-0.143	1.084	-1.756	-1.839
Bob	-1.715	-1.097	1.602	-1.2
Bonin	1.246	2.954	0.17	0.456
Demi-Lune	-1.964	-2.268	0.381	1.614
Eau claire	-0.133	1.835	-0.053	0.804
Fraser	-1.224	-1.348	-0.372	1.076
Gervais	1.113	0.739	-1.113	-0.31
Gilmour	-1.526	2.524	-1.286	0.174
Girard	0.391	2.636	0.66	0.134
Guilbeault	2.687	-1.692	0.933	0.824
Heney	-0.612	-0.407	-2.813	0.232
Jean Venne	4.434	2.531	0.48	0.83
Kalalla	-1.828	-2.055	1.763	-0.806
La Peche	-0.109	1.792	1.51	-0.9579
Letourneau	2.609	-1.475	-1.006	-1.031
Loups	0.939	-0.642	-1.495	-1.127

APPENDIX VII (continued)

Noir	1.195	-2.901	-1.764	1.552
Orignal	-1.795	-0.539	-0.317	1.291
Perdrix	-2.332	-0.092	-1.171	-0.698
Pink	-3.088	0.748	3.017	-1.197
Profond	-2.008	3.35	0.973	-0.389
Renaud	4.794	0.559	2.127	-0.189
Trois Monts	2.992	-2.936	2.008	0.051
Truite	-4.037	-1.504	0.79	0.058
Twin	1.607	1.087	-2.113	-1.573
Vase	1.421	-3.506	1.567	-0.134
Vert	-1.642	-1.714	-1.126	0.658
Victoria	-0.17	-0.555	-0.111	-1.163

APPENDIX VIII A) Importance of each component retained in the redundancy analysis. B) Loadings of each retained variable in the components retained in the redundancy component analysis.

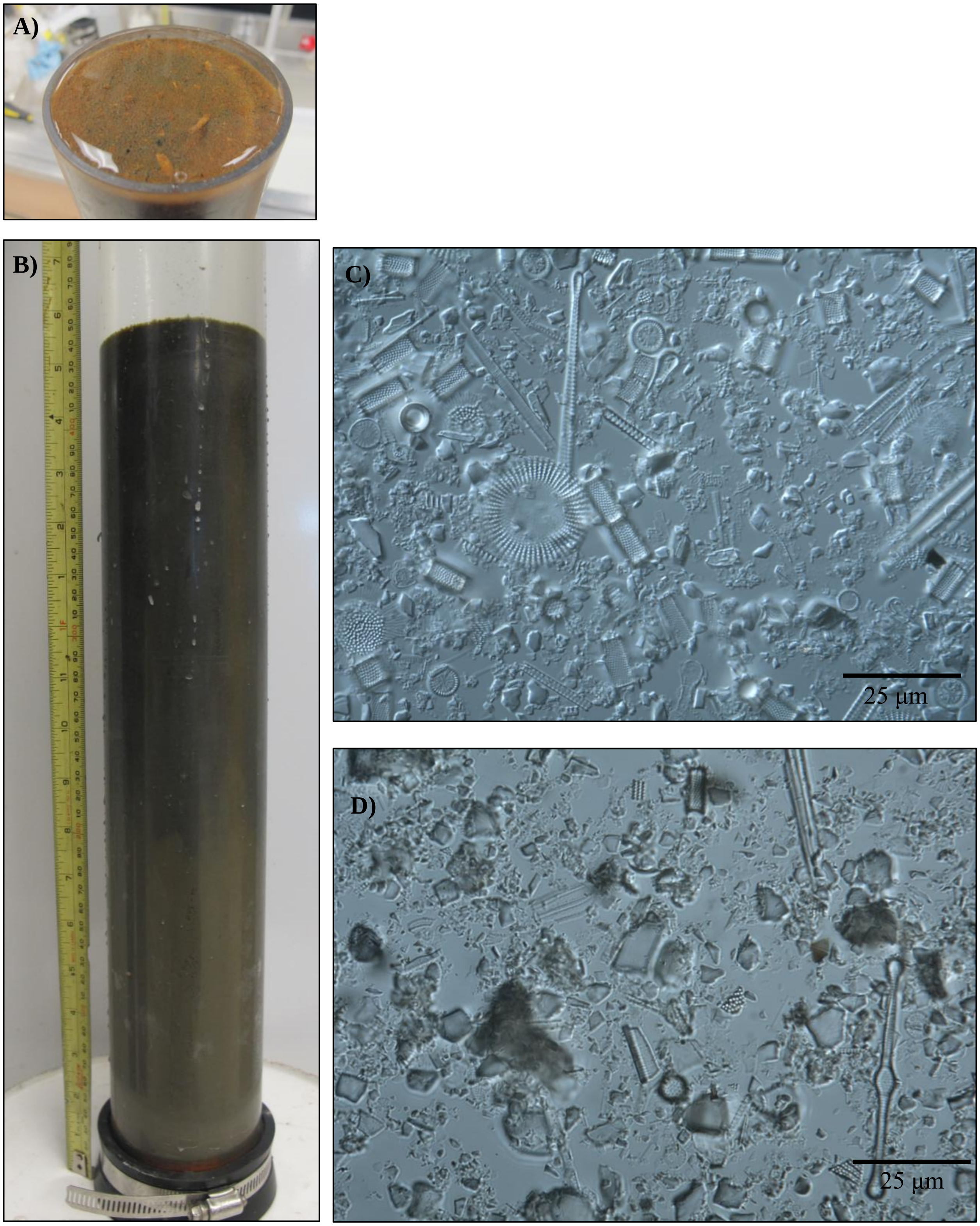
A)	RDA1	RDA2	RDA3	RDA4
Eigenvalue	0.0678	0.0526	0.0108	0.0051
Proportion explained	0.1614	0.1252	0.0256	0.0106
Cumulative proportion	0.1614	0.2866	0.3122	0.3122

B)	RDA1	RDA2	RDA3	RDA4
MD	-0.9162	-0.2478	0.0977	-0.2993
Fe_d	0.3918	-0.7981	-0.1960	0.4137
MP	-0.4019	0.5447	0.3526	-0.6462
TP	0.2801	0.0703	0.7668	0.5732

APPENDIX IX Diatom assemblage from surficial sediments of Lake Vert, dominated by planktonic species. Species present include *Cyclotella comensis*, *Cyclotella bodanica* and *Cyclotella cyclopuncta*.

APPENDIX X Diatom assemblage from surficial sediments of Lake Renaud, dominated by benthic species. Species present include *Aulacoseira nivaloides*, *Cyclotella bodanica*, *Tabellaria flocculosa*, *Staurosira construens*, *Staurosira construens var. venter*, *Pseudostaurosira brevistriata*, *Planothidium rostratum*, *Cavinula pseudoscutiformis*, *Placoneis explanata* and *Eunotia pectinalis*.

APPENDIX XI A) Surficial sediments of Heney Lake sediment core prior to extraction; B) side view of Heney Lake sediment core prior to extrusion; C) diatom assemblage of Heney Lake surficial sediments; D) Diatom assemblage in Heney Lake in pre-European settlement period (15-16 cm). Species present include *Tabellaria flocculosa* and *Aulacoseira subarctica*.



APPENDIX XII Scanning Electron Microscope images of the more buoyant *Cyclotella comensis* (upper panel) and the tubular shaped, fast sinking, *Aulacoseira subarctica* (lower panel), from Heney Lake surficial sediments.