

Paleolimnology of the Lake of the Woods southern basin

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ABSTRACT

To quantify the environmental history of the southern basin of Lake of the Woods (Ontario, Manitoba and Minnesota), seven core locations were selected for retrospective analyses. Primary goals were to determine pre-European settlement conditions and track the timing and extent of anthropogenic impacts and remediation. Sediments were dated using isotopic analyses and fossil remains, in concord with other stratigraphic indicators (organic and inorganic materials, sedimentation rates, other biological entities), were used to reconstruct the ~150-year history of the lake. Diatom assemblages were assessed from sediment intervals and inferred trophic conditions in the profiles were derived using a regional diatom-based model for Minnesota lakes. Nutrient reconstructions indicated a period of cultural eutrophication throughout much of the 20th century. Despite a known reduction in anthropogenic nutrient flux to the lake in recent decades, there has been no apparent reversal in eutrophication in the pelagic system. Contemporary observations indicate that blooms of blue-green algae are becoming a greater problem. It appears that legacy nutrient recycling and other environmental drivers are maintaining the current condition of pelagic nutrient enrichment. Sedimentary analyses also indicated that physical changes to the lake resulting from warming may be contributing in small part to the recent reorganization of algal assemblages.

BACKGROUND AND INTRODUCTION

Lake of the Woods (LoW; 49° N, 95° W) is a large (385,000 ha), shallow (mean depth = 7.9 m) lake occupying parts of the Canadian provinces of Ontario and Manitoba and the U.S. state of Minnesota (Fig. 1). It is a waterbody of current and historical, international importance.

Historic and present land uses around the lake include agriculture, urbanization, forestry, mining and recreation including tourism. Most of the human activity around Lake of the Woods in the 1800s occurred in the northern, Canadian portion, particularly in the watershed of the Winnipeg River. However, beginning in 1905 European settlement became notable in Lake of the Woods County, Minnesota, in the watershed of Zippel Bay (Baldwin 1926). Forest clearance in northern Lake of the Woods County began around this time, and by 1915 a number of roads and drainage ditches had been constructed in the county. By 1925 crops and farmland totaled approximately 9,000 ha and 56,000 ha, respectively. Human manipulation of water levels on LoW was initiated with the construction of the Norman Dam by 1895 at the outlet near Kenora. Detailed historical data on anthropogenic activities in the LoW catchment are further summarized by Clark et al. (2014).

Several anthropogenic stressors have impacted the freshwater systems in the temperate regions of North America. In particular, cultural eutrophication is a major environmental concern, as nutrient additions may dramatically alter lake and river conditions, such as increased primary production (e.g., algal blooms) and hypolimnetic anoxia (Kira 1993). With increased primary productivity, there is a subsequent increase in suspended and sedimenting organic matter (Nürnberg 1995). Microbial decomposition of this organic matter often leads to the depletion of dissolved oxygen (DO), eventually leading to a state of anoxia. Anoxia is a serious problem because it can cause the displacement and death of fish and benthic invertebrates, and it facilitates the release of reduced substances from the sediments, including potentially toxic substances and biologically available phosphorus (Nürnberg 1995). Other negative ramifications associated with eutrophication include decreased availability of water for drinking, irrigation and industrial purposes, taste and odor problems, decreased recreational value and decreased

biological diversity and aesthetic value (Carpenter et al. 1998). From a lake management perspective, finding solutions to these undesirable consequences requires a working knowledge of how lakes have responded to, and in some cases, recovered from, eutrophication events. This retrospective knowledge is critical to ensure cost effective and ecologically sound lake management protocols (Smol 2002).

Dense algal blooms have been reported in the southern portion of LoW since the early 1800s (McElroy and Riggs 1943), so it is expected that the lake is naturally productive. Rainy River, which contributes an estimated 70% of the total water inflow, is an important source of nutrients to LoW. Examination of nutrients from various sources indicates that the Rainy River contributes two thirds of the annual phosphorus load to the lake. In the past much of this nutrient load came from excess agricultural applications and erosion of natural supplies in soil. Awareness of the potential for deleterious environmental damage has resulted in widespread action to reduce anthropogenic pollutant flux to aquatic systems, such as that outlined in the Clean Water Act, which was enacted in 1972 (Litke 1999). Due to remedial attention nutrient loads to the lake from the Rainy River have decreased in recent decades (Hargan et al. 2011, The Lake of the Woods Water Sustainability Foundation 2011). Despite this remediation of the nutrient flux, there is a perceived water quality decline in recent years due to large populations of toxin-producing cyanobacteria (Hargan et al. 2011). It may be that the historical phosphorus loads manifesting in the basin sediments may be available for ongoing algal production through the process of internal loading (remobilization of phosphorus from the lake sediments). Especially under conditions of warmer and longer ice-free seasons in the lake (Pla et al. 2005) we need to figure out the long-term conditions and trajectory of change in terms of nutrient and algal characteristics (Rühland et al. 2010).

Another stressor of concern to LoW is erosion. As much of the watershed was deforested in the late 1800s through the early 1900s, followed by ditching for agricultural drainage later in the 20th century, erosion of the catchment became an important factor for bank stability, water quality and sediment accumulation rate issues. An increased water level due to damming caused erosion of the southern shoreline (Houston Engineering 2013). Previous paleolimnological work on Zippel Bay (Reavie & Baratono 2007) indicated substantial anthropogenic increases in sediment load, but a similar impact on the southern basin of LoW is uncertain.

Long-term environmental data are critical to proper management of LoW, but as is generally the case, long-term monitoring data are incomplete. In cases where long-term data are available, these data tend to only cover recent time periods, generally after environmental problems were realized. Even with an exemplary, ongoing monitoring program for LoW (e.g., Clark et al. 2014, Pla et al. 2005), there are few data to adequately describe the long-term impacts human activities have had on environmental quality, and the sorts of impacts that may result from future human activities and environmental changes are unknown. Hence, management recommendations are lacking because a time-integrated assessment of the overall environmental status of LoW is needed. Paleolimnology offers a means to fill these data gaps in ecological history.

Paleolimnology is the historical study of inland aquatic systems. In most cases, a core is taken from the sediments of a limnological system, and the fossils, geological and chemical signals that are preserved in the core are investigated to reveal the ecological history of the aquatic system and the surrounding landscape (Smol 1992). The evidence preserved in the sediments can be used to provide quantitative and qualitative reconstructions of important physical, chemical and biological trends that have resulted from natural and anthropogenic factors.

An incredible amount of information is stored in the biological fossil record of sediments. Algae are the most popular of paleolimnological indicators because they respond to stressors including nutrient and salinity loading, siltation and factors affecting water transparency (such as erosion and exotic species) (Smol and Stoermer 2010). The most commonly used biological indicators in paleolimnological analyses are the diatom algae (class Bacillariophyceae). They are ubiquitous, diverse, have a short turnover rate and have narrow tolerances to environmental conditions (Dixit et al. 1992). Diatoms are especially useful because their siliceous cell walls (frustules) leave diagnostic fossil remains that allow past species assemblages to be identified from the sedimentary record. There has been a rapid increase in the use of indices based on diatoms in aquatic ecosystems. A recent study (Reavie et al. 2006) indicated that diatoms can provide robust indicator models for several water quality variables. Moreover, the diatom assemblages better reflected impacts from watershed stressors (e.g., agriculture, urban development, point sources) than directly-measured water quality parameters such as nutrients, water clarity and chloride, demonstrating that the diatoms were better suited to integrating environmental conditions than snapshot water quality measurements. The fossil diatom species present in sedimentary profiles from Lake of the Woods can provide a detailed archive of past environmental information that would otherwise be unavailable. A paleolimnological assessment offers pre-settlement baselines, environmental trends, and the timing and magnitude of changes related to human activities. By reconstructing the long-term degradation and subsequent rehabilitation (if evident) of environmental quality, two important questions could be answered:

- What has been the extent of past ecological change, and how close have rehabilitation efforts come to returning water quality to pre-human settlement conditions?
- What is the trajectory of the inferred environmental trends, and is there evidence that additional remedial action might be needed?

In the Minnesota region, paleolimnological applications have targeted several modern-versus-pre-European reconstructions of environmental parameters (e.g., Heiskary and Swain 2002, Ramstack et al. 2003). In particular, Minnesota lake sediment records have been used in the characterization of nutrient records (e.g., Edlund and Engstrom 2001, Kingston et al. 2004). Lake of the Woods has been investigated using various paleolimnological techniques (e.g., Pla et al. 2005, Yang and Teller 2005), with other studies currently in progress. To add to this body of information, a paleolimnological analysis of the lake was undertaken based on seven sediment cores collected throughout the shallow, southern basin. Data were related to known historical impacts and remediation efforts. The paleolimnological information obtained in this study will provide baseline data for sound management decisions and remediation goals for future efforts to maintain and restore the quality of ecological systems in Lake of the Woods.

The Lake of Woods Water Sustainability Foundation includes a consortium to determine the phosphorus budget for Lake of the Woods. Major goals are to determine the sources and amounts of phosphorus entering the lake and to develop water quality models. It is hoped that a better understanding of why algal blooms are increasing will support management, and paleolimnology will put these modern conditions in a long-term context. This technical report is part of a larger, integrated study to support management of LoW (Clark et al. 2014). In particular, results from this work will directly support the development of a nutrient budget for the LoW system.

METHODS

Sediment Sampling

Seven sediment profiles were collected to represent human history in the region (at least 150 years) so that pre- and post-remedial trends may be inferred. Sediment profiles were collected from the main basin (Big Traverse Bay, 2 stations), Muskeg Bay, Buffalo Bay, Sabaskong Bay, Little Traverse Bay and Big Narrows (Fig. 1).

Sediment cores were taken from the ice surface from February 28 through March 1 2012 using a piston corer, which is specially designed for sampling lake sediments (Glew et al. 2001). Surface sediment profiles were collected in approximately 1-m sections which incorporated the sediment-water interface. Loose surface sediments in the piston cores were sectioned on-site into 1-cm intervals using a close-sectioning extruder. The unsectioned core portions were kept cool and transported to the lab for core splitting, photography and subsampling. In the lab, cores were split lengthwise in their tubes using a band saw. Stratigraphic information (including sediment color, texture and anomalous entities) was recorded and the cores were photographed.

Each core half was then sectioned into 1-cm intervals and recombined in vials. Samples were stored using clean techniques for additional analyses and long-term storage.

Inorganic and organic content, sediment dating, metals accumulation

Loss on ignition. Organic and inorganic loss-on-ignition (LOI) analyses followed Dean (1974). Sediment water content was determined from weight lost following oven drying of sediments at 100 °C for 24 hours. Weight loss after placing in a muffle furnace at 550 °C for two hours was used as an estimate of organic content. Weight loss after placing the remaining material in a muffle furnace for 2 hours at 1000 °C provided an estimate of carbonate content that is used to reflect inorganic carbonates (largely calcium carbonate) (Boyle 2001).

Sediment dating. Cores of lake sediments were analyzed for excess lead-210 (^{210}Pb) activity to determine age and sediment accumulation rates for the past 100-150 years. ^{210}Pb was measured at 15-20 depth intervals in each core through its granddaughter product ^{210}Po , with ^{209}Po added as an internal yield tracer. The polonium isotopes were distilled from 0.5-3.0 g dry sediment at 550 °C following pretreatment with concentrated hydrochloric acid (HCl) and plated directly onto silver planchets from a 0.5 N HCl solution (modified from Eakins and Morrison 1978). Activity was measured for $1-6 \times 10^5$ s with ion-implanted surface barrier detectors and an Ortec[®] alpha spectroscopy system. Unsupported ^{210}Pb was calculated by subtracting supported activity from the total activity measured at each level; supported ^{210}Pb was estimated from the asymptotic activity at depth (the mean of the lowermost samples in a core). Dates and sedimentation rates were determined according to the constant rate of supply (CRS) model (Appleby and Oldfield 1978) with confidence intervals calculated by first-order error analysis of counting uncertainty (Binford 1990). Dating analyses were performed by scientists at the Science Museum of Minnesota's St. Croix Watershed Research Station.

Diatoms and other microfossils

Sample digestion, plating and analysis. Diatom frustules were cleaned of organic material by digestion to allow identification of diatom species. Weighed sediment subsamples (~0.5 wet g) were diluted with 130 mL deionized water and treated with 20 mL concentrated nitric acid on a hot plate. Samples were heated at approximately 100 °C until 20 mL remained. Then, 25 mL

hydrogen peroxide (30% solution) was added using a catalyst of potassium dichromate and again heated until 10-15 mL remained. Samples were rinsed eight times in centrifuge tubes by diluting and spinning down the samples at 2000 rpm for 10 minutes. Coverslips were prepared using the Battarbee (1986) method, pouring a known subsample diluted in water into dishes holding coverslips, preparing two slides per sample interval by adhesion with Naphrax[®] mountant. Naphrax[®] has a high refraction index and allows better distinction of the morphological features of the diatoms. The Battarbee method allowed for the quantitative assessment of absolute diatom abundance and accumulation rates.

Diatoms were identified and enumerated using an upright light microscope at 1000-1250 × magnification with oil immersion. At least 400 diatom valves were counted per slide. To allow for discussion and taxonomic refinement, representative specimens were photographed with a Lumenera Infinity 2 digital camera. Diatom taxonomy and enumeration techniques were practiced and an initial taxonomic photo database was created to aid in consistent diatom identification. Diatoms were identified to the species level or higher using standard floras and iconographs, including Hustedt (1927-1966), Patrick and Reimer (1966, 1975), Krammer and Lange-Bertalot (1986, 1988, 1991a, b), Cumming et al. (1995), Reavie and Smol (1998), Camburn and Charles (2000) and Fallu et al. (2000). Diatoms were counted when more than 50% of the valve was present or when a distinct valve fragment was present (e.g., central area of *Amphora libyca* or valve end in *Asterionella formosa*).

To aid in temporally grouping historical trends in the diatom assemblages, cluster analysis was applied to the diatom assemblages in each fossil profile using the “chclust” function in R (statistical package version 2.15.2, R Development Core Team 2010) using the rioja package (version 0.8-7, Juggins 2012). The CONISS algorithm (Grimm 1987) was used to perform clustering constrained to vertical stratigraphy, providing a dendrogram for each diatom profile.

Although diatoms were the primary indicators used, siliceous remains including chrysophyte stomatocysts, phytoliths, plates of testate amoebae and sponge spicules were also enumerated to provide additional ecological information. Most species of the chrysophyte algae (Chrysophyceae) endogenously form siliceous resting stages called stomatocysts (Duff et al. 1995). In general, the presence of stomatocysts in the sedimentary record characterizes oligotrophic conditions (Smol 1985), and cysts have been applied to paleolimnological issues such as eutrophication (e.g., Carney and Sandgren 1983) and acidification (e.g., Duff and Smol 1991). Testate amoebae (Rhizopoda, also known as testaceans and thecamoebans) are freshwater protozoans that are common in soils, streams, lakes and wetland environments containing dense vegetation such as macrophytes and mosses (Warner 1990; Tolonen 1985; Loeblich and Tappan 1964). Phytoliths are microscopic siliceous bodies that form in stems, leaves, roots and inflorescences of plants. Following the disintegration of organic tissues, the phytolith microfossils are preserved in sedimentary records (Rovner 1971). Spicules are the microscopic skeletal elements of sponges, and these typically siliceous bodies are preserved in sedimentary records following the disintegration of organic tissues. Spicules and plates of amoebae were not sufficiently abundant in samples to consider in the results of this study.

Diatom-inferred environmental conditions. Diatom calibration and training sets have become powerful tools for paleoecological reconstruction. The development of weighted averaging regression and calibration introduced a method of quantitative reconstruction of historical environmental variables (Birks et al. 1990a, b). The method uses a transfer function developed

from a training set of modern diatom assemblages and their relationships to environmental gradients. The transfer function can be applied to historical diatom assemblages in sediment cores to mathematically reconstruct specific environmental variables. The weighted averaging method is statistically robust and based on ecologically sound organismal responses (ter Braak and Prentice 1988, Birks et al. 1990b), and the approach has been used successfully in reconstructing a wide variety of environmental parameters including pH, total phosphorus (TP), dissolved organic carbon (DOC) and salinity (e.g., Anderson 1989, Fritz et al. 1991, 1999, Dixit et al. 1992, Reavie et al. 1995).

To develop a set of useful diatom indicators, a diatom transfer function is derived by relating diatom species assemblages in a training set of samples (e.g., from lakes, river reaches, coastal locales) to an environmental variable of interest (e.g., total phosphorus or nitrogen, pH, chloride, suspended solids) from a particular region (Charles 1990, Juggins and Birks 2012). The transfer function consists of species coefficients (e.g., environmental optima and tolerances for each species) that can be used to infer quantitative information about the variable of interest, based on the relative abundance of each species in a sample assemblage. Past total phosphorus (TP) concentrations were inferred from the fossil diatom assemblages using the diatom-based reconstructive model that has been developed (Ramstack et al. 2003) and progressively updated (Heiskary and Swain 2002, Edlund and Kingston 2004, Reavie et al. 2005, Paterson et al. 2007) for Minnesota Lakes. Weighted averaging (WA) calibration and regression were used to derive a diatom-based model using R and the package *rioja*. *Rioja* quantitatively reconstructs environmental variables using weighted averaging of the diatom species and their associated environmental optima and tolerances. The diatom transfer function was derived by relating diatom species assemblages in the training set samples to measured TP. Past TP concentrations were inferred from the fossil diatom assemblages using the transfer function, which estimates TP based on the TP optima of the fossil taxa, weighted by their relative abundance. The full model is known to have good performance statistics (Reavie and Juggins 2011), and details of diatom-based transfer function development and application are provided by Juggins and Birks (2012).

Several methods were applied to ensure the diatom-based TP training set model was appropriate for application to the diatom assemblages in the LoW cores. Analog analysis was performed using the R package *analogue* (Simpson and Oksanen 2013) by matching of assemblages among modern samples from the training set and fossil (downcore) diatom assemblages from this study (Flower et al. 1997, Simpson et al. 2005). The method identifies the closest analogs of fossil samples from the modern training set to assess the reliability of diatom-inferred data. The R script generates a pairwise dissimilarity matrix for the modern training set, and a second matrix containing the pairwise dissimilarities between each fossil sample and each sample in the training set. Analogs were determined using Bray-Curtis dissimilarity (Bray and Curtis 1957). Dissimilarities of the ten “closest” (i.e. most similar) modern assemblages to each fossil assemblage were compiled to assess how well each fossil assemblage was represented in modern collections.

A canonical correspondence analysis (CCA) constrained to TP was used to evaluate relationships between fossil samples and the modern TP gradient. The residual distance of fossil diatom assemblages to the TP axis provided a measure to assess “lack of fit” to TP. First, using the R package *vegan* (Oksanen et al. 2013), CCA determined extreme residual distances from the TP axis (i.e. axis 1) by ordinating modern diatom sample assemblages constrained to TP. TP effectively becomes the first CCA axis and the distance of each modern sample score from this

axis reflects its “fit” to TP. Fossil samples were then run passively in CCA using the “timetrack” function in the R package analogue (Simpson and Oksanen 2013). Fossil samples were positioned, by means of transition formulae, with respect to the TP axis. Fossil samples with residual distances greater than the 95% confidence limits of the training set sample scores were considered to have “poor fit” to TP, and so inferred TP from those assemblages would be considered unreliable.

Additional testing was applied according to Reavie et al. (2014a) to determine whether DI-TP was appropriate for downcore analysis in LoW. Multivariate ordinations were performed using the R package “vegan” (Oksanen et al. 2013). For diatom-environmental analyses in the training set, redundancy analysis (RDA), the constrained form of principal components analysis (PCA), was performed to condense the complex training set data into summary variables (axes) that capture the majority of environmental variation (Juggins and Birks 2012). To track the historical trajectory of diatom assemblages as it related to the training set, sedimentary assemblages were projected on the RDA containing the suite of training set diatom data and environmental variables. We then calculated the correlation coefficient for fossil DI-TP versus corresponding axis 1 sample scores from the unconstrained PCA of the sedimentary diatom assemblages. We would expect this value to be high (i.e. an absolute value close to a proportion of 1.0) if downcore assemblages were strongly related to changes in TP (Juggins et al. 2013).

RESULTS AND DISCUSSION

Dating

Total ^{210}Pb in recent (core-top) sediments ranged from ~3 pCi/g in Buffalo Bay to 23 pCi/g in Big Traverse 3, and down-core declines were largely smooth and monotonic (Fig. 2, left panel). The profiles had fairly typical decay curves, exhibiting exponential declines in ^{210}Pb concentrations. Supported ^{210}Pb was well defined in all cores and allowed for accurate calculation of dates according the CRS model (Fig. 2, center panel). Overall, these profiles would be expected in lakes with consistent sediment accumulation regimes, and we are confident that relatively undisturbed sedimentary profiles were obtained. Date-depth relationships were somewhat divergent among locations with the highest overall accumulation rates in Sabaskong Bay (Fig. 2, right panel). Sediment accumulation rates varied among the seven cores, but in general all cores indicated a gradual increase in sediment accumulation rate from ~20 cm through ~5 cm depth. Buffalo Bay was an exception, representing over 100 years in the upper 7 cm of sediment, owing to dense, highly inorganic sediments with low porewater content (Fig. 3). Above ~5 cm in all cores no notable increase or decrease in sediment accumulation rates is apparent, suggesting possible stabilization in erosion.

Sediment content

Loss-on-ignition (LOI) analysis (Fig. 3) provided retrospectives of the various sediment components. With the exception of Buffalo Bay, water content was typically in excess of 68%, predictably decreasing downcore as sediments became more compressed. A substantially higher proportion of organic content in the Muskeg core indicates higher organic input, which is balanced by lower inorganic content. Organics increased since human development, most markedly so in the last few decades. Aside from the most recent few years which shows an increase in all cores, little trend was observed for the proportion of carbonates in the sediments, although Little Traverse Bay had a lower carbonate load overall than the other locations.

Accumulation rates of all materials indicate a gradual increase in accumulation in the last ~100 years, suggesting some additional input due to increased erosion of catchment materials. There has been a levelling off of inorganic accumulation in the last decade. However, during this time rates of carbonate accumulation continued to increase in the Little Traverse, Big Narrows, Muskeg and Sabaskong cores, all locations that are nearer to coastlines. Again, Buffalo Bay was an exception with a lower proportion and accumulation of carbonates and higher proportion of inorganic materials in the last ~60 years, suggesting that Buffalo Bay sediments reflect eroded materials more so than the other cores. Additional discussion of accumulation rates is provided in the context of their microfossil profiles.

Diatoms and other entities

We encountered approximately 400 diatom taxa and several additional entities in the Lake of the Woods cores. Additional entities included the stomatocysts (resting stages) of chrysophyte algae and plant phytoliths which were sufficiently abundant to plot quantitatively. Large amounts of data are presented for each lake; not all profile data presented are addressed in this discussion, but instead we focus on key trends for interpretation.

Although there was a trend of increasing accumulation of siliceous microfossils likely related to increasing productivity overall (Fig. 4), the general long-term decline in the ratio of stomatocysts to diatoms also suggests a shift to higher productivity as chrysophytes tend to be more abundant in oligotrophic conditions (Smol 1985). Combined with diatom trends, chrysophyte fossil trends suggest long-term, continued eutrophication in the system. The increase in phytolith accumulation in four of the core sites nearer to shore (Little Traverse, Big Narrows, Muskeg, and possibly Sabaskong) are indicative of increasing soil erosion which would carry and deposit soil-borne and riparian phytoliths to the sediments.

A casual observation of the diatom profiles (Figs. 5-11) indicates that all cores had similar dominant diatom assemblages. In particular, a pre-impact dominance of *Aulacoseira islandica* was the norm across all sites. This taxon is a spring bloomer that is well recognized from large, shallow lakes (e.g., Reavie et al. 2014b). Its presence suggests a naturally mesotrophic condition (Reavie et al. 2014a) as well as the wind-driven physical control on limnology, which is needed to ensure the heavy valves of *Aulacoseira* remain suspended in the water column. Pre-impact subdominants included *Aulacoseira subarctica* (another winter-spring diatom) and *Aulacoseira granulata*, which is a summer diatom that is known to prefer higher nutrient conditions (Reavie et al. 2014a).

Reorganization of the diatom communities at all core locations occurred gradually. In general, changes started to occur in the early 20th century with a slow decline in *A. islandica* to be displaced by *A. subarctica*, *A. granulata* and *Aulacoseira ambigua*. The gradual increase in diatom accumulation rates (Fig. 4) indicates increasing production along with changes in the assemblages. More substantial reorganization of the diatom assemblages occurred in the last two to three decades, with a shift to planktonic taxa that are known to reflect eutrophic conditions: *Stephanodiscus medius*, *Stephanodiscus minutus*, *Stephanodiscus parvus*, *Stephanodiscus* sp. 10, *Cyclostephanos dubius* (Reavie et al. 2014a). These taxa were responsible for the unique clustering of the upper intervals of each core, reflecting a unique modern assemblage. Buffalo Bay, which had sedimentary assemblages more highly represented by benthic, epipsammic taxa (e.g., *Pseudostaurosira brevistriata*) had a less prominent recent shift to eutrophic taxa, but still indicated a relative increase in the high-nutrient *C. dubius*.

Cluster analyses among diatom profiles showed remarkably similar results for relative abundance data, with the exception of Buffalo Bay. A “recent” cluster generally occurred starting around ~1990–2000 through to the present. These uppermost clusters represented the increasing relative abundance of taxa indicating higher nutrients (e.g., *C. dubius*, *S. sp. 10*; Reavie et al. 2014a) and taxa that may indicate climate-induced changes (e.g., *Discostella stelligera*; Saros et al. 2012).

Profiles of diatom accumulation rates (Figs. 5-11, lower panels) indicate increased diatom accumulation since ~1990, particularly for the high-nutrient taxa mentioned above (*C. dubius*, *S. sp. 10*, *S. minutus*, *S. parvus*). This trend further suggests increasing productivity, although the sharp increase in accumulation rates in the uppermost interval of each nearshore core may be misleading. Those recent samples may contain temporally constrained diatom accumulations from seasonal blooms. Samples from deeper in the cores can represent two or more years of diatom accumulation, and so they better reflect prevailing diatom accumulation conditions.

Diatom-based TP reconstruction

The first step in reconstructing past nutrients was to provide assurance that application of the Minnesota diatom model (Reavie et al. 2005) is appropriate for the Lake of the Woods fossil assemblages. Analog comparisons of the Lake of the Woods diatom assemblages with modern assemblages indicate that deeper assemblages tended to have higher similarities to model data (Appendix A), although in all cases there were modern (model) samples that were sufficiently similar to each fossil sample to justify application of the TP model. Further, all fossil sample scores were within the 95% distance from the TP axis, indicating good fit to TP for all fossil samples.

Then, a thorough, passive evaluation of the fossil assemblages relative to a RDA of the model training set was used to determine whether long-term trajectories responded along a gradient that is well-defined by phosphorus (Reavie et al. 2014a; Appendix B). This analysis indicated that all fossil diatom profiles except Big Traverse 3 were significantly related to the TP gradient as defined by the modern samples, indicating that most of the diatom histories were driven to some degree by phosphorus in the lake’s water column. Although the Big Traverse 4 record was significantly related to phosphorus, it had the second-lowest correlation between the fossil species gradient and DI-TP (Appendix B, bottom panels). This indicates that water quality conditions in deeper sites that are farther from shore may be less determined by phosphorus, and that nearshore locations are more directly influenced by anthropogenic nutrients.

Although the timing and quantity of diatom-inferred changes in TP varied among cores, the general trend was one of increasing phosphorus concentrations starting around the 1930s or 1940s (Fig. 12; Appendix A, far right panels). Big Traverse 3, Big Traverse 4 and Sabaskong cores indicated a relatively small increase in TP, in the range of ~15 - 25 $\mu\text{g/L}$. Muskeg, Little Traverse and Big Narrows had a greater increase, from a pre-impact concentration of approximately 10 $\mu\text{g/L}$ to 30 $\mu\text{g/L}$ at the top of the cores. Buffalo Bay had a unique shift from the mid-20s to almost 40 $\mu\text{g/L}$. Error bars indicate the error associated with model inference of TP (Appendix A), but overall trends are that of persistent eutrophication. These long-term TP inferences have been included in the latest phosphorus budget for LoW (Edlund et al. 2015)

GENERAL DISCUSSION

Although there were variations in the paleolimnology of the seven locations in Lake of the

Woods, several general statements can be made about the southern lake system as a whole. A significant disruption that is evident in the paleoecological record was the transition from a mesotrophic to a meso-eutrophic system, particularly in the last few decades. Even without an increase in nutrient flux to the lake (Hargan et al. 2011), eutrophication appears to be continuing, as further evidenced from recent, substantial blooms of cyanobacteria. Although there was a recent increase in diatoms from the *Cyclotella sensu lato* complex (*Cyclotella*, *Discostella*) in the Big Traverse cores, the increase we observed was far more subtle than that observed in the deeper, northern basins (Rühland et al. 2010). The stratigraphic shift toward more *Cyclotella* in recent decades is generally correlated with lake warming (Rühland et al. 2008), so factors other than warming are probably greater drivers of the recent changes in diatoms in the southern basin.

Accumulation of organic materials, total sediments and phytoplankton abundance have increased and species composition changed to suit the new, enriched environment. Increased sediment supplies may be related to shoreline erosion resulting from climatological factors, but greater study is needed to better quantify such drivers. Nutrient-related impacts on the lake appear to be more pronounced in areas closer to shore, and it may be that offshore changes are confounded by lake-wide influences that include warming.

It was well-known that past activities in and around Lake of the Woods (e.g., agriculture, ditching) decoupled the naturally-occurring phosphorus cycling for the region. Large mass transfers of phosphorus (and nitrogen) into concentrated areas of agricultural production resulted in regional decoupling of phosphorus cycling rates from carbon. In pristine and managed environments phosphorus transfers in soils and water are largely biologically mediated, while in fertilized agricultural systems phosphorus inputs are often significantly greater than outputs in produce, so biological controls can become overwhelmed (Sharpley et al., 2006). This leads to shifts in the stoichiometry of nutrients (ratios of P, N, and C) delivered to downstream ecosystems. Such is probably the case for Lake of the Woods, although it was anticipated that controls on use of phosphorus and better management of runoff would alleviate cultural eutrophication in the lake. From this study it is obvious that, despite the known reduction in nutrient flux to the southern basin of Lake of the Woods, nutrient enrichment and associated algal blooms continue to be a problem. Paleolimnological records of algae, inferred nutrients and sediment accumulation, and recent observations of extensive algal blooms, confirm these issues. Legacy phosphorus archived in the lake sediments may be masking or buffering the positive effects of contemporary conservation measures.

Phosphorus-driven eutrophication may be driven by increasing accumulation of organic material as we have noted in recent decades. Increased inputs of labile carbon in organic materials from terrestrial or other sources can fuel higher rates of microbial respiration in sediments. As a result, microbial degradation of organic matter releases P and enhances oxygen depletion, resulting in reductive dissolution of iron oxyhydroxides, which release sediment-sorbed P. Increased export of organic C has the potential to increase the mobilization of legacy P stores. While there is no confirmation of the relationship between organic accumulation and P mobilization in LoW, a potential remedial recommendation would be to reduce overall flux of materials (nutrients and organic materials carrying labile carbon) to the lake to pre-impact levels.

Although LoW is a unique system, comparable remedial failures have occurred elsewhere. Loch Leven is a shallow (mean depth 3.9 m) lake that is relatively large by UK standards (13.3 km² surface area). The lake has a long and well-documented history of eutrophication problems.

Efforts were made to restore water quality during the late 1970s to early 1990s by reducing the external P inputs by about 60% (May et al., 2012). This was mainly achieved by reducing industrial inputs and by upgrading sewage treatment works. Farmers were also encouraged to change their management practices and use less fertilizer in the watershed. In-lake winter and spring total P concentrations responded rapidly by falling about 75% in winter and 60% in spring compared with pre-management levels. Nevertheless, summer concentrations of P remained high, with concentrations actually increasing (Sharpley et al. 2013). Overall this suggested a switch in dominance from external to internal P loading in the lake. After ~8 years the summer P peaks started to decline, but remained higher than expected and hoped.

Even with lower nutrient standing loads in managed lakes, recent observations indicate other confounding factors can contribute to continued eutrophication. In Sweden's largest lake, Lake Vänern, phytoplankton biomass has significantly increased since the 1980s while total phosphorus and inorganic nitrogen concentrations have significantly decreased (Weyhenmeyer & Broberg 2014). For oligotrophic Lake Vänern it was determined that increasing lake temperatures and alkalinity were more important for phytoplankton growth than total phosphorous and nitrogen concentrations. While Lake Vänern and Lake of the Woods are comparable in size, and so may experience similar atmospheric deposition and warming regimes, whether they are experiencing analogous changes is uncertain due to their differences in depth, geography and trophic status. Whether phosphorus is declining in the Lake of the Woods pelagic system has not been confirmed and evidently Lake of the Woods alkalinity is decreasing (DeSellas et al. 2009). Given known warming as evidenced by the increasing ice-free season (Clark et al. 2014), and the recent increase in diatoms known to respond to warming-induced changes in the lake (e.g., *Discostella*; Rühland et al. 2010) such a possibility is worth considering.

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FIGURE CAPTIONS

Fig. 1 Map of core locations in Lake of the Woods.

Fig. 2 Lead-210 activities and depth-date relationships and sediment accumulation rates in sediment cores collected from Lake of the Woods. Basin-specific line plots are identified by their corresponding color in the heading.

Fig. 3 Proportions and accumulation rates of sedimentary components in cores collected from Lake of the Woods based. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Basin-specific line plots are identified by their corresponding color in the heading.

Fig. 4 Downcore sediment trends for diatoms, chrysophyte stomatocysts and phytoliths from Lake of the Woods. Data are presented as accumulation rates ($/\text{cm}^2/\text{y}$) or relative abundance (%) to illustrate trends. The ratio of stomatocysts to diatoms is presented as a unitless ratio. Basin-specific line plots are identified by their corresponding color in the heading.

Fig. 5 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Big Traverse 3 sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 50,000 cells/ cm^2/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 6 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Big Traverse 4 sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 50,000 cells/ cm^2/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 7 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Muskeg Bay sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 200,000 cells/ cm^2/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 8 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Sabaskong Bay sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 200,000 cells/ cm^2/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 9 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Little Traverse Bay sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 200,000 cells/ cm^2/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 10 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Big Narrows Bay sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 200,000 cells/cm²/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 11 Stratigraphies of the relative frequencies (top) and accumulation rates (bottom) of dominant diatom taxa identified in the Buffalo Bay sediment core from Lake of the Woods. Interval dates represent a constant-rate-of-supply age model applied to the ^{210}Pb data. Taxa shown occurred at a relative abundance of at least 2 % (top) or 20,000 cells/cm²/y (bottom) in at least one sample. A dendrogram illustrating depth-constrained cluster analysis of the diatom assemblages is plotted on the right.

Fig. 12. Compiled diatom-inferred total phosphorus concentrations based on sedimentary assemblages from Lake of the Woods. Basin-specific line plots are identified by their corresponding color in the heading.

Fig. 1

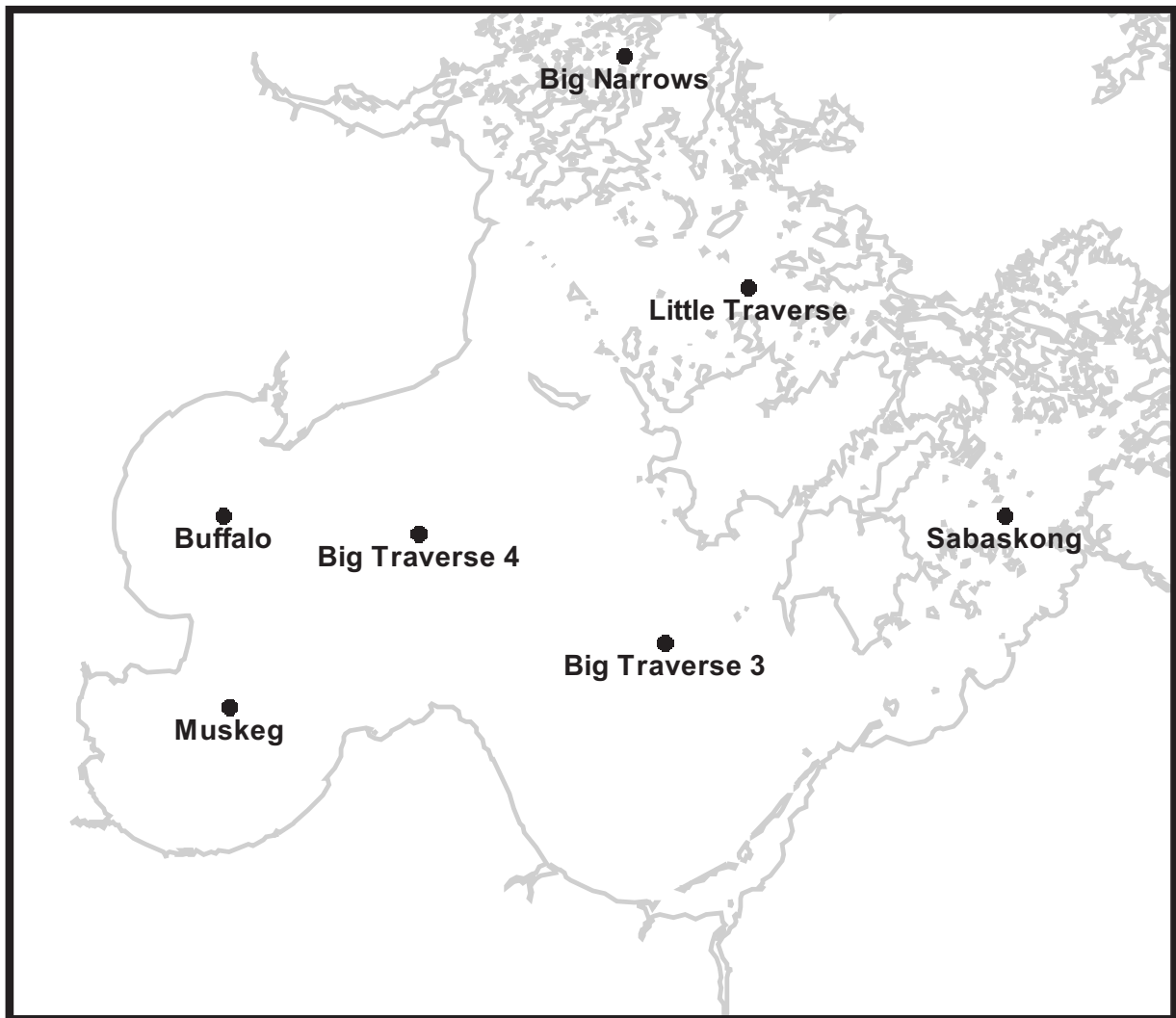


Fig. 2

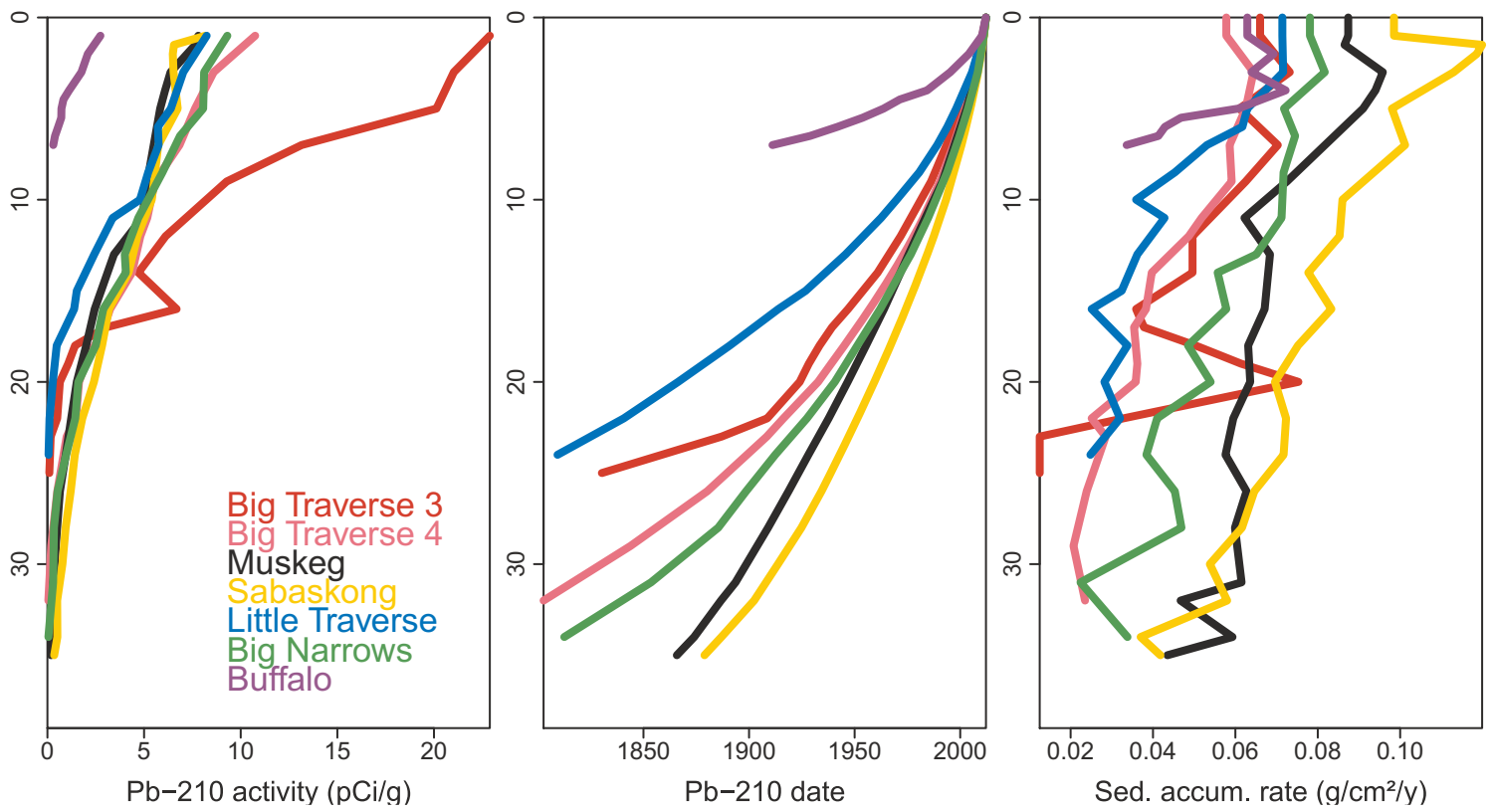


Fig. 3

Big Traverse 3
Big Traverse 4
Muskeg
Sabaskong
Little Traverse
Big Narrows
Buffalo

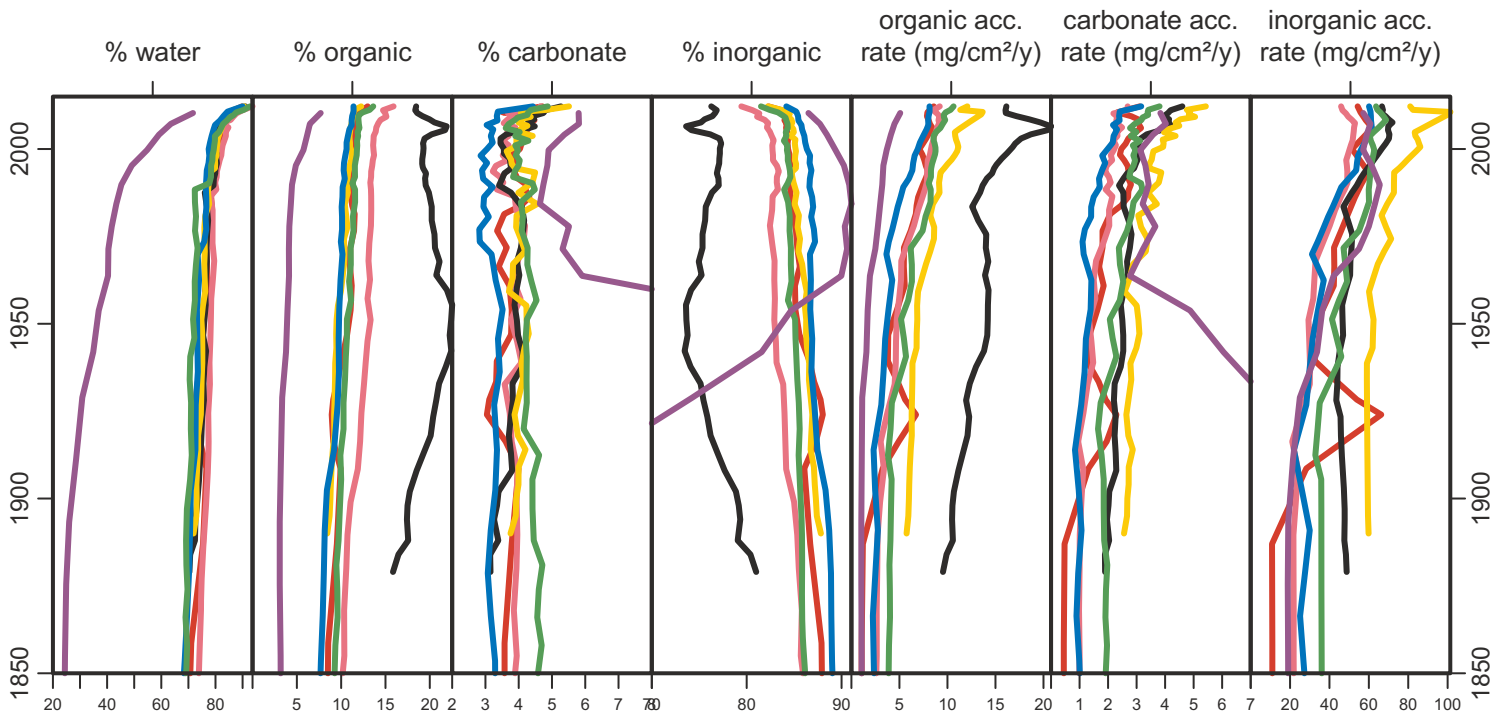


Fig. 4

Big Traverse 3
Big Traverse 4
Muskeg
Sabaskong
Little Traverse
Big Narrows
Buffalo

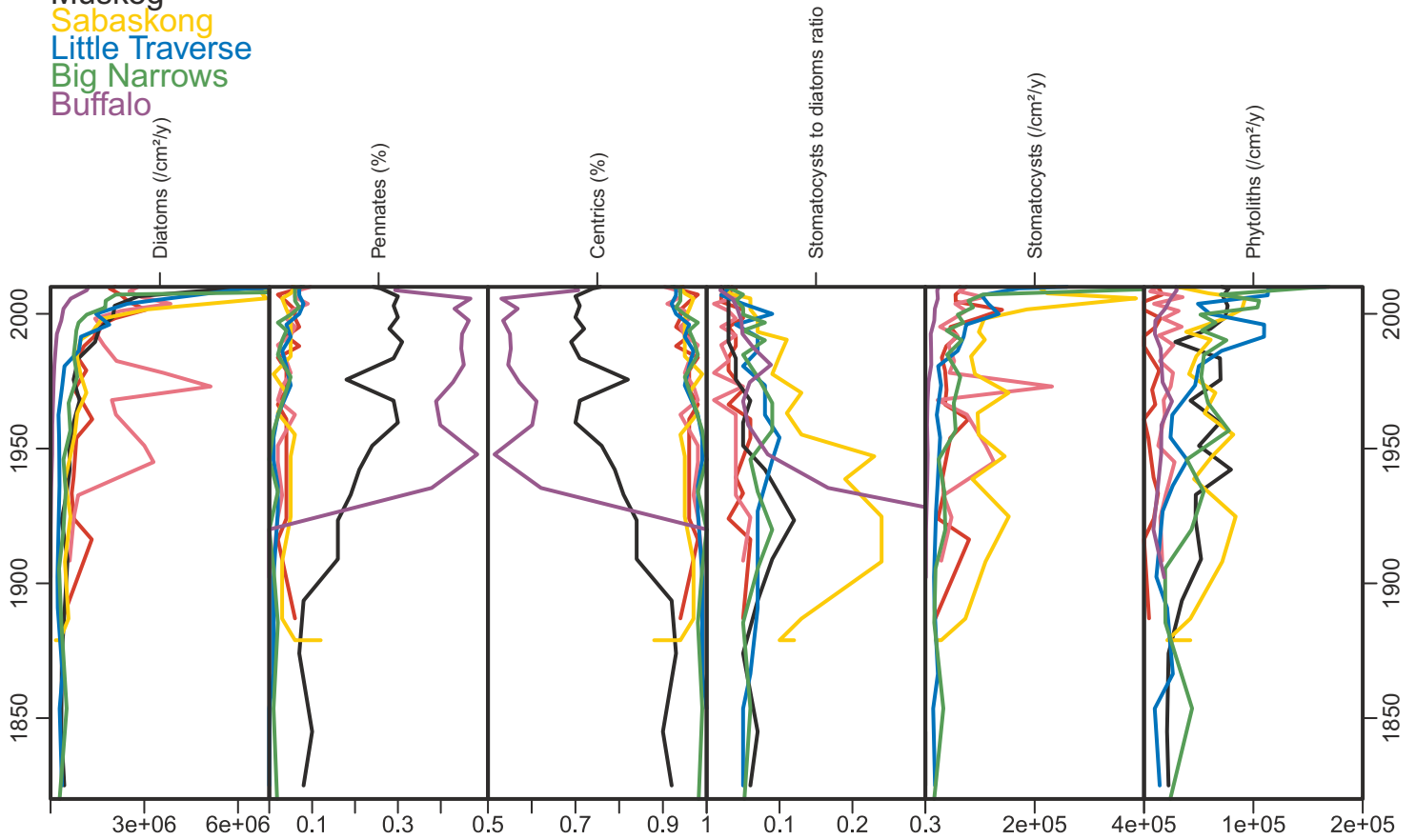


Fig. 5

Big Traverse 3

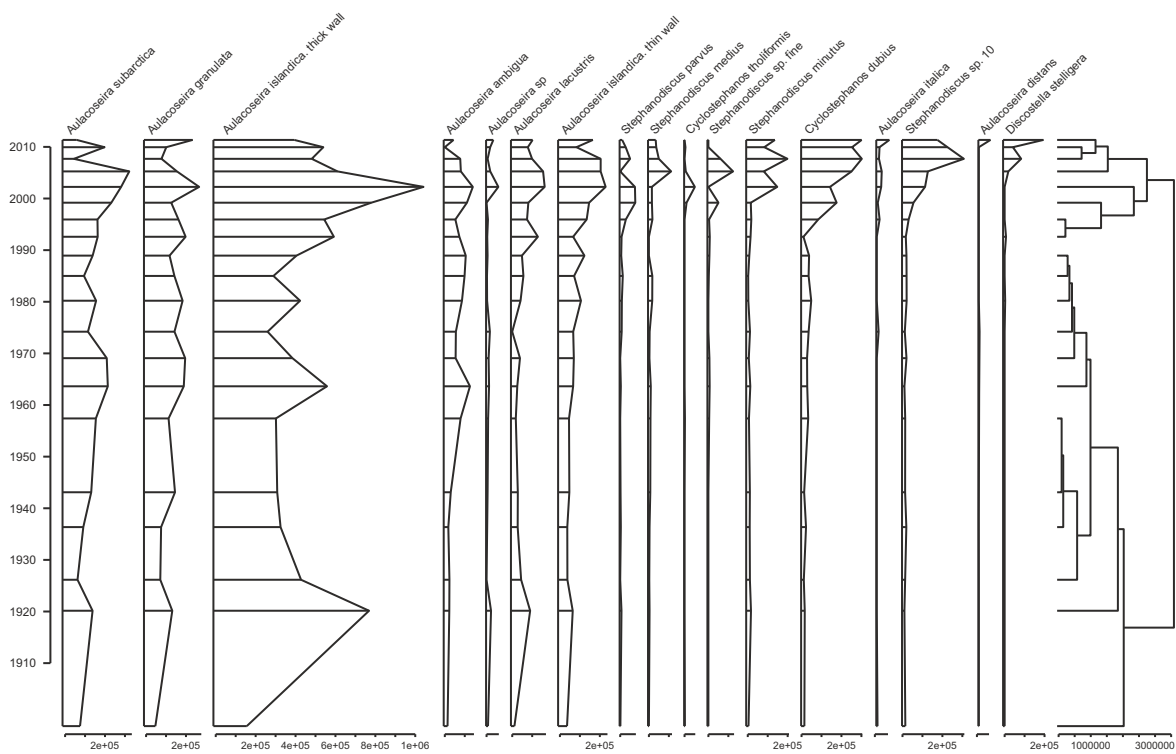
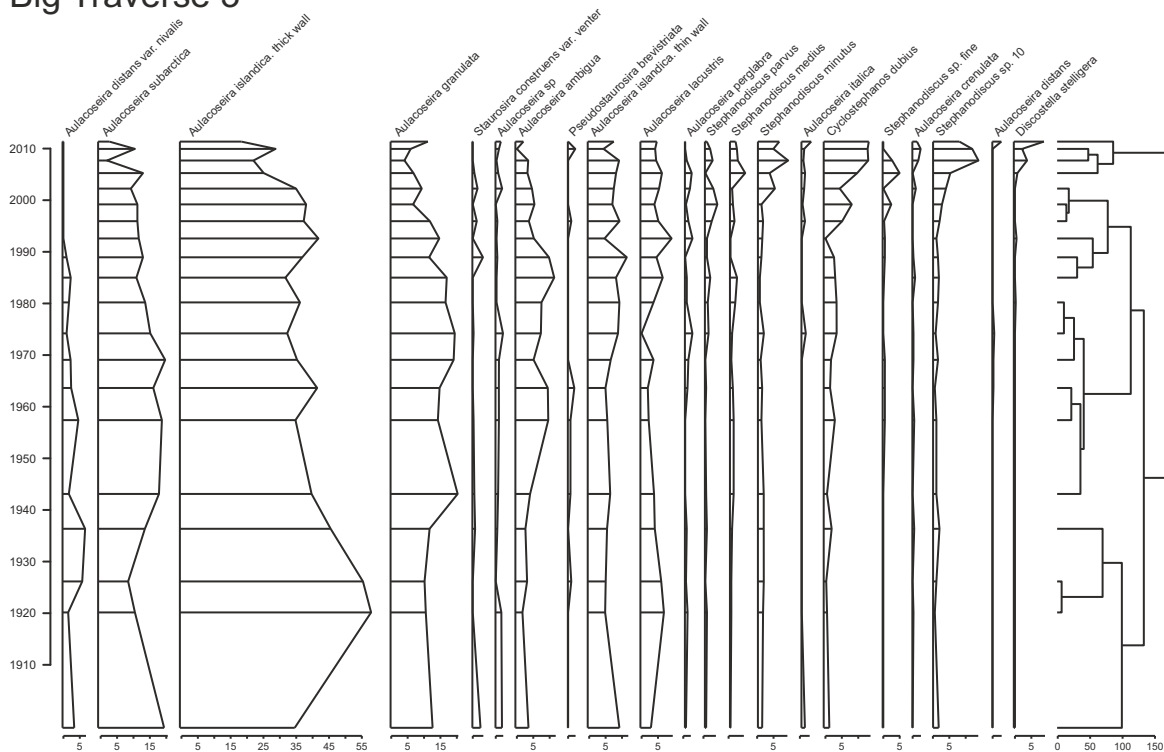


Fig. 6

Big Traverse 4

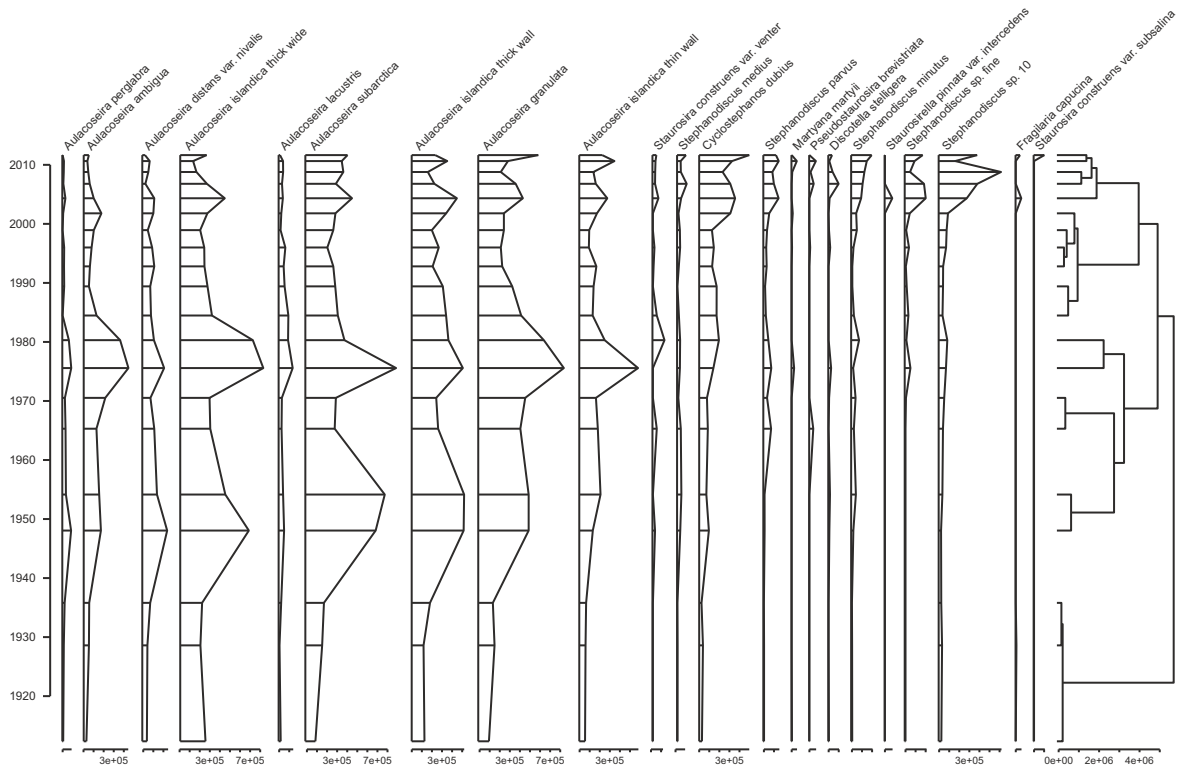
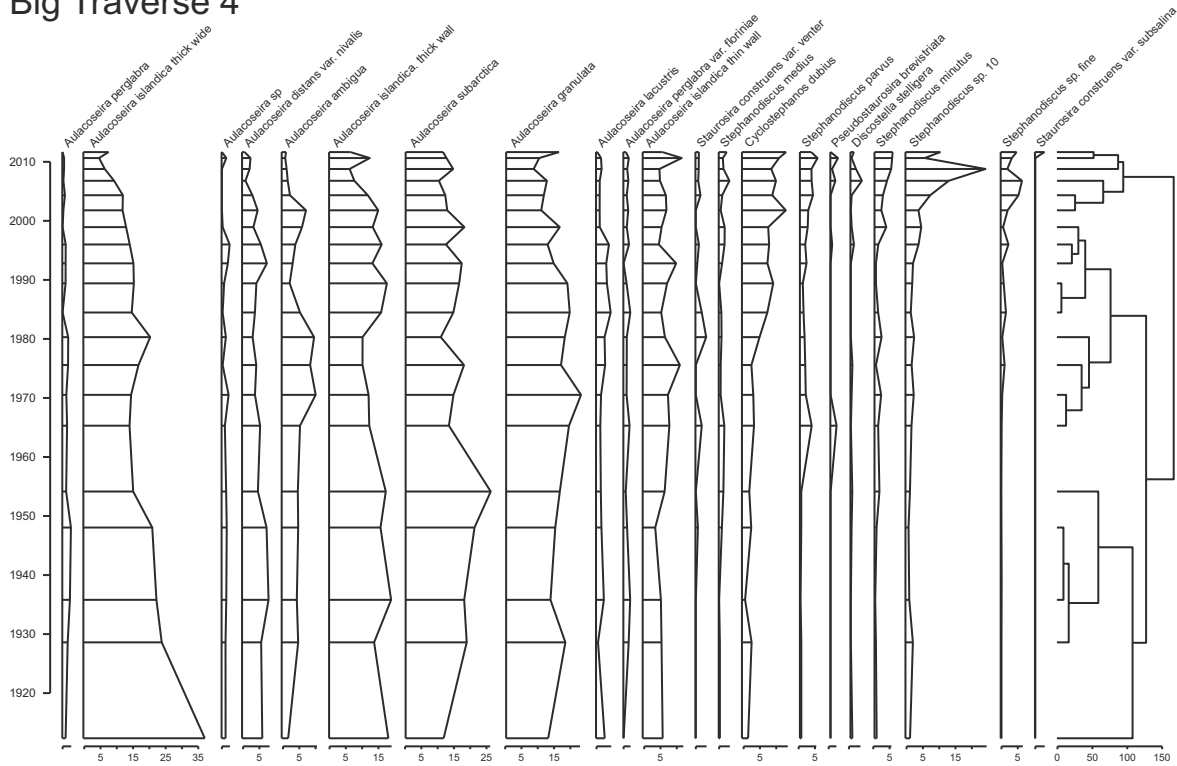


Fig. 7

Muskeg

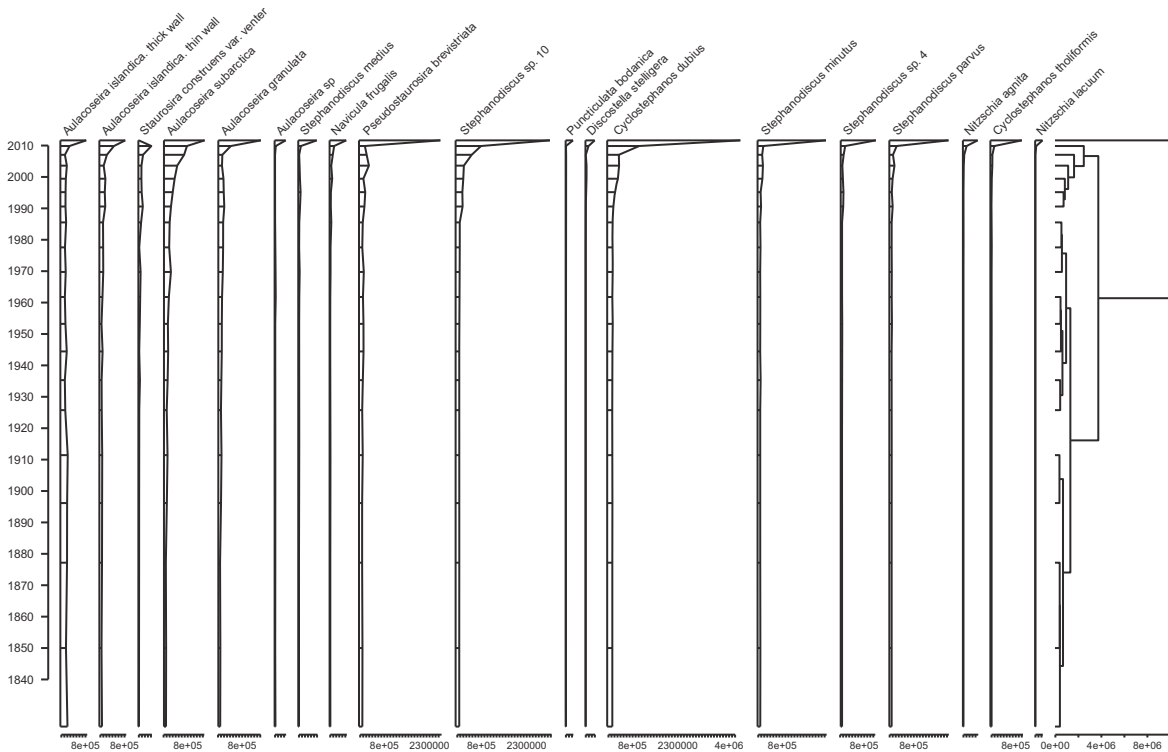
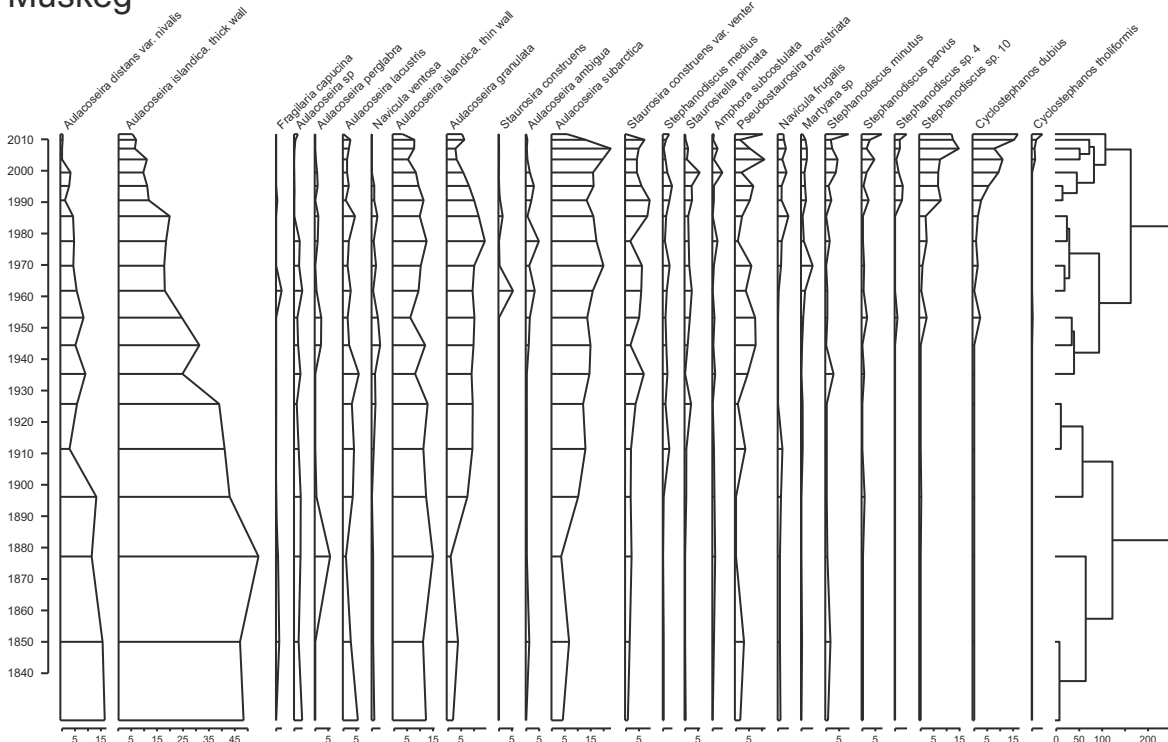


Fig. 8

Sabaskong

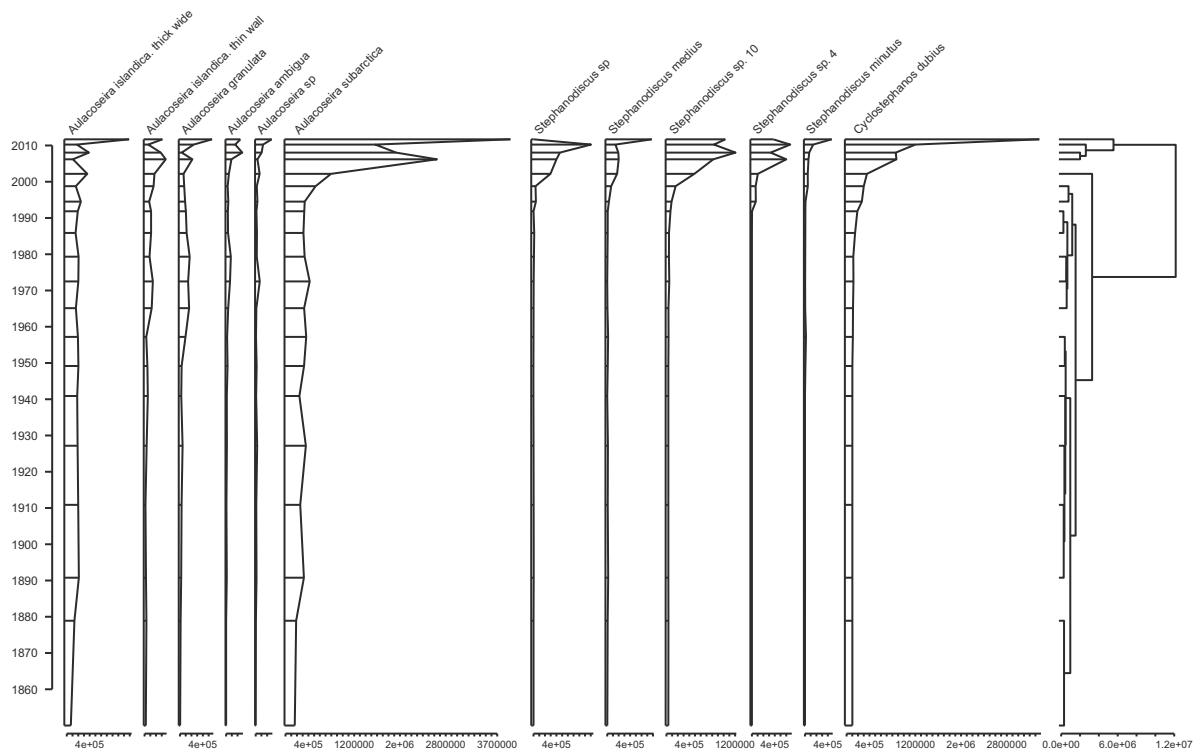
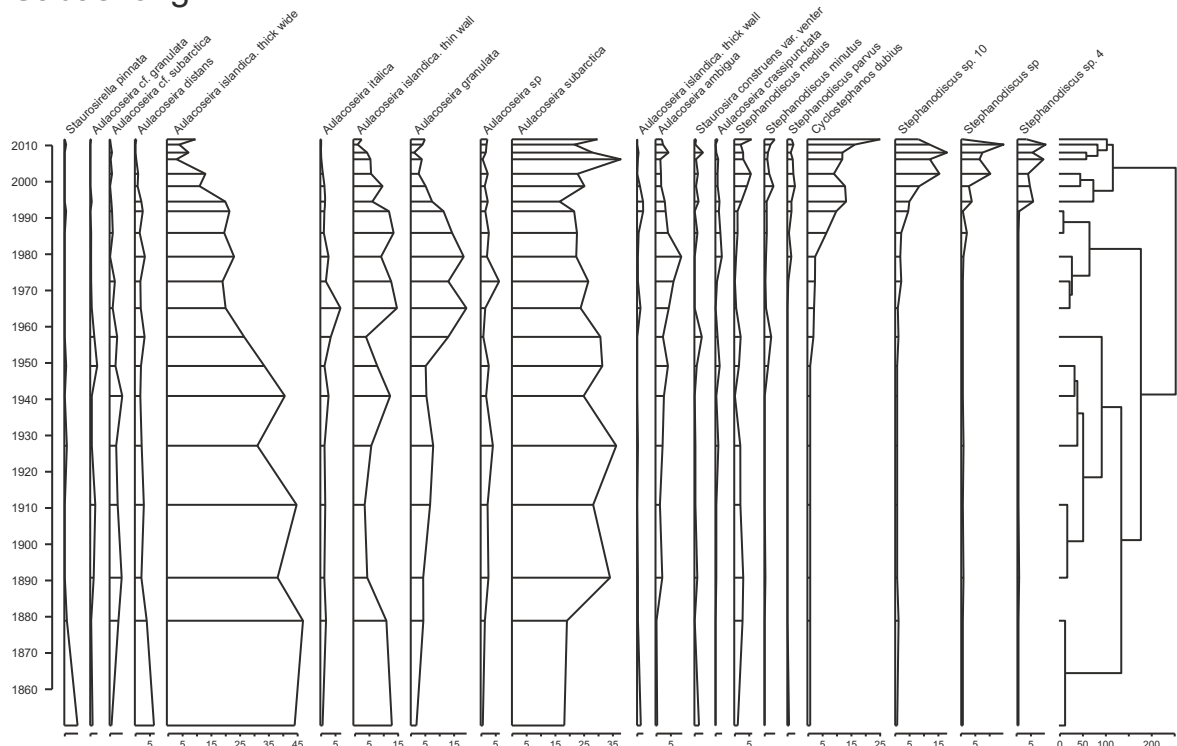


Fig. 9

Little Traverse

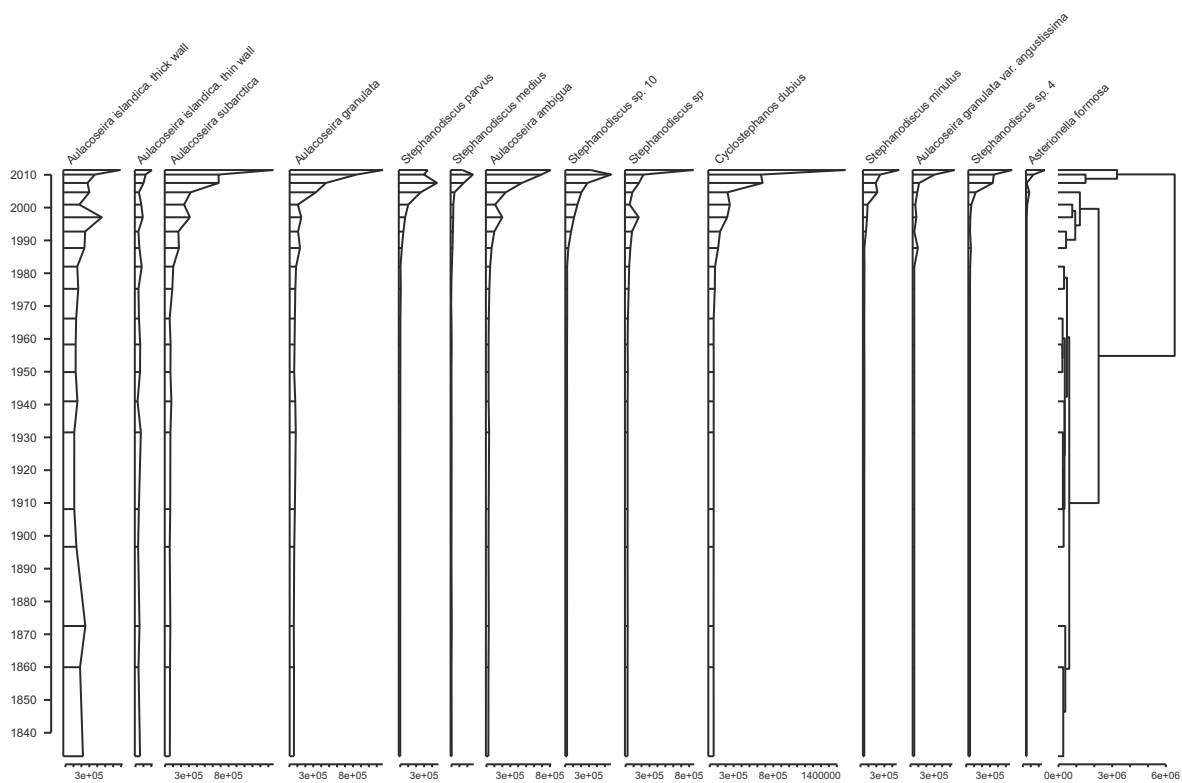
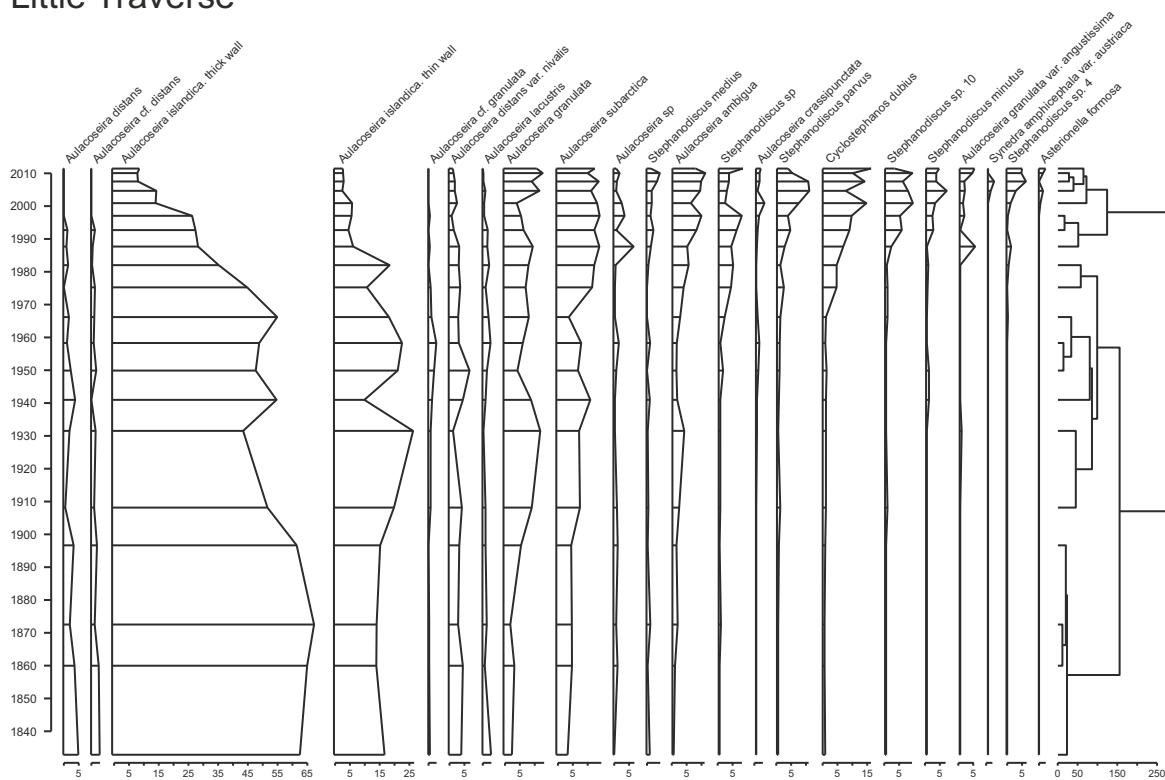


Fig. 10

Big Narrows

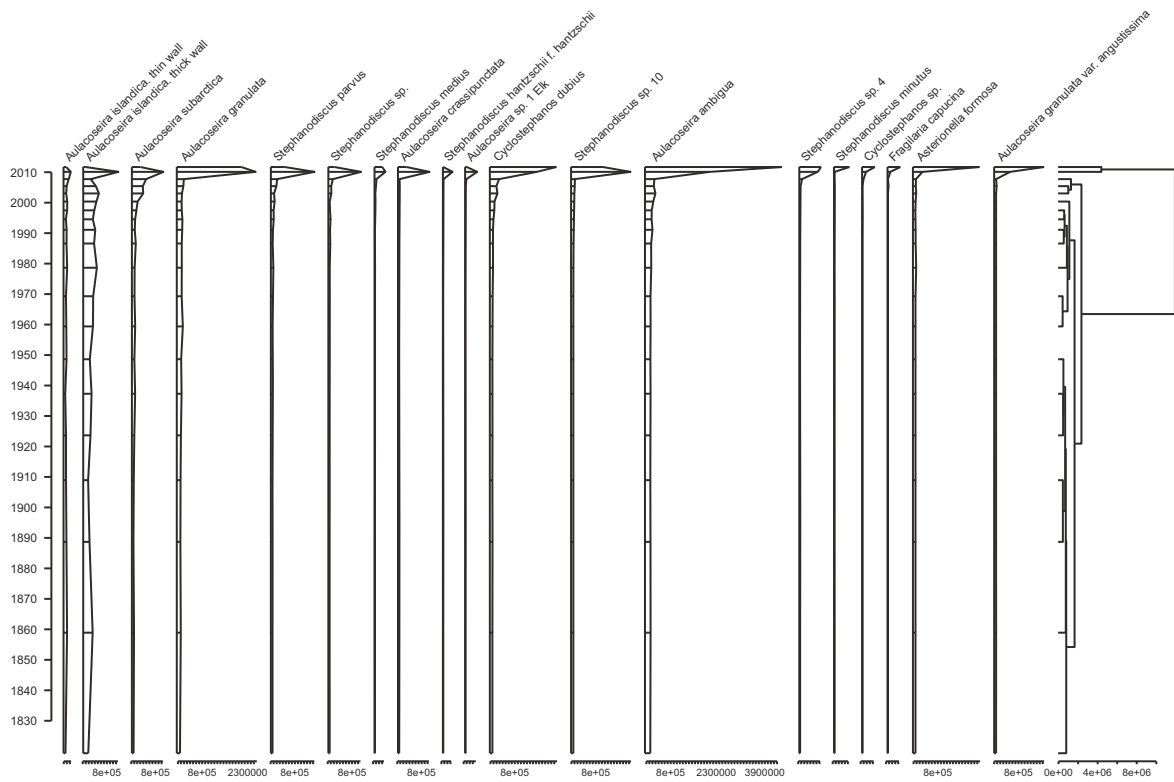
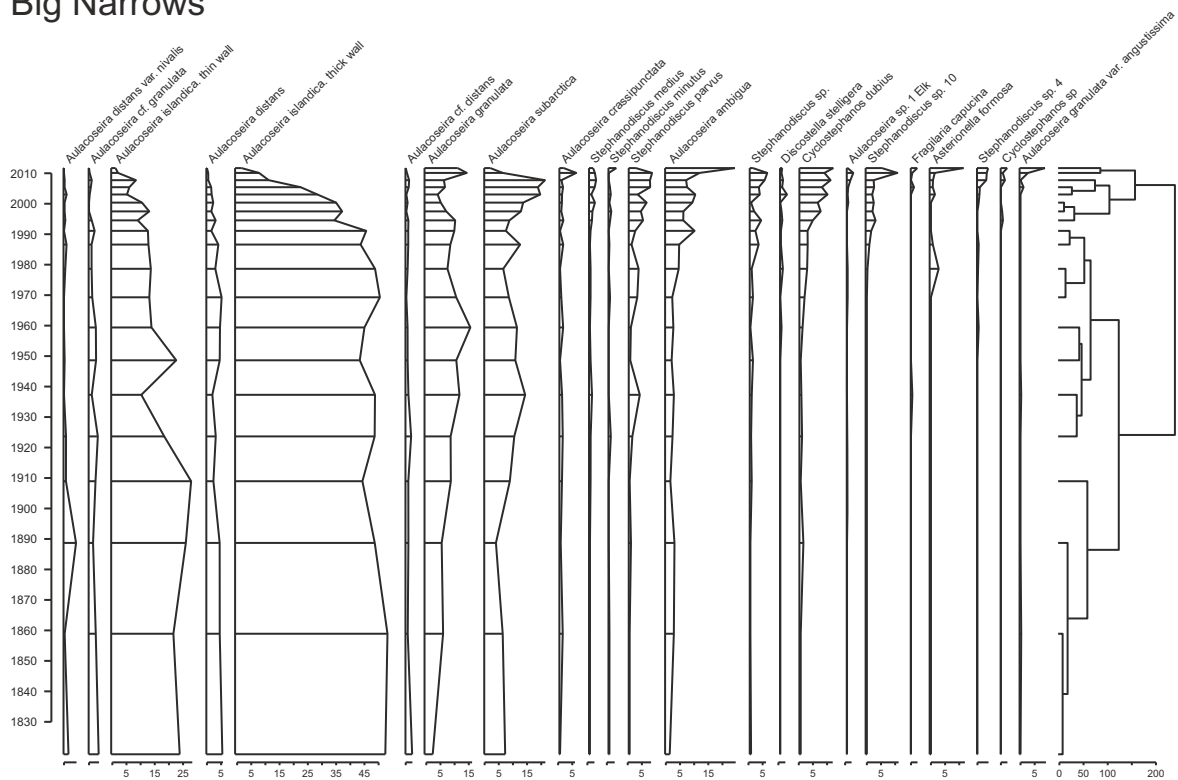


Fig. 11

Buffalo

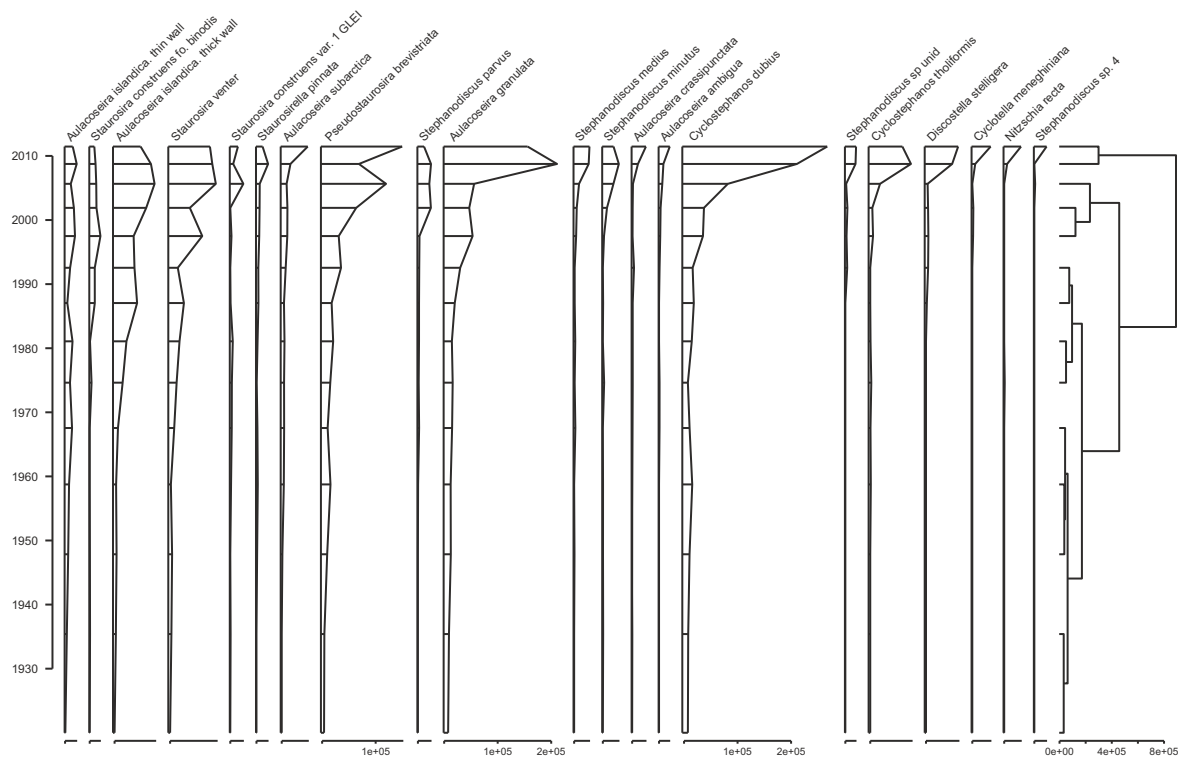
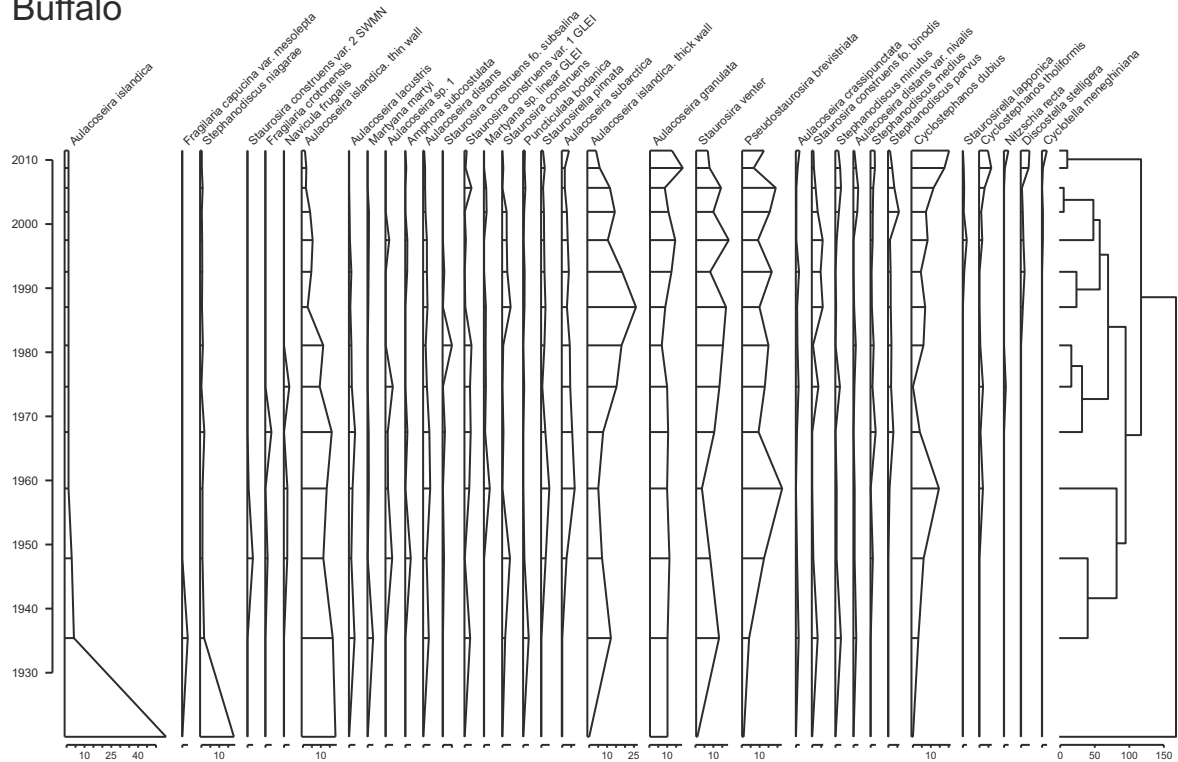
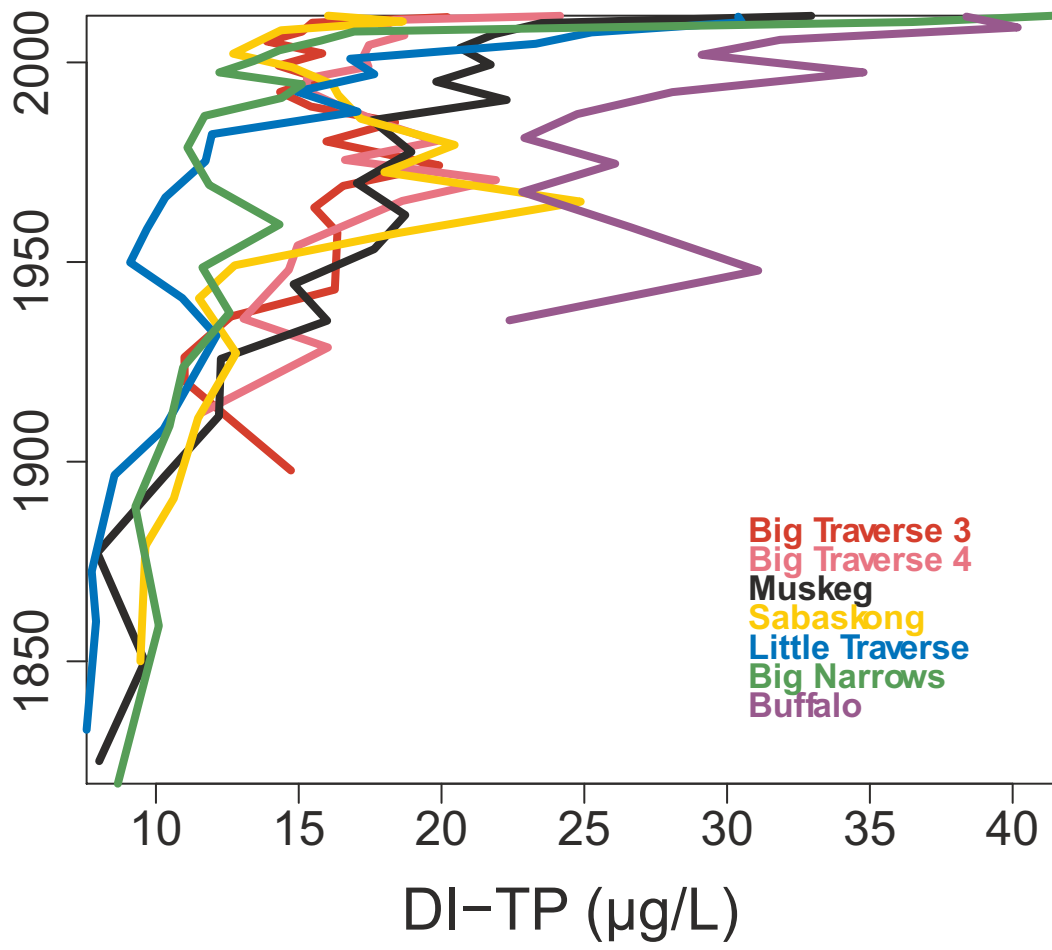


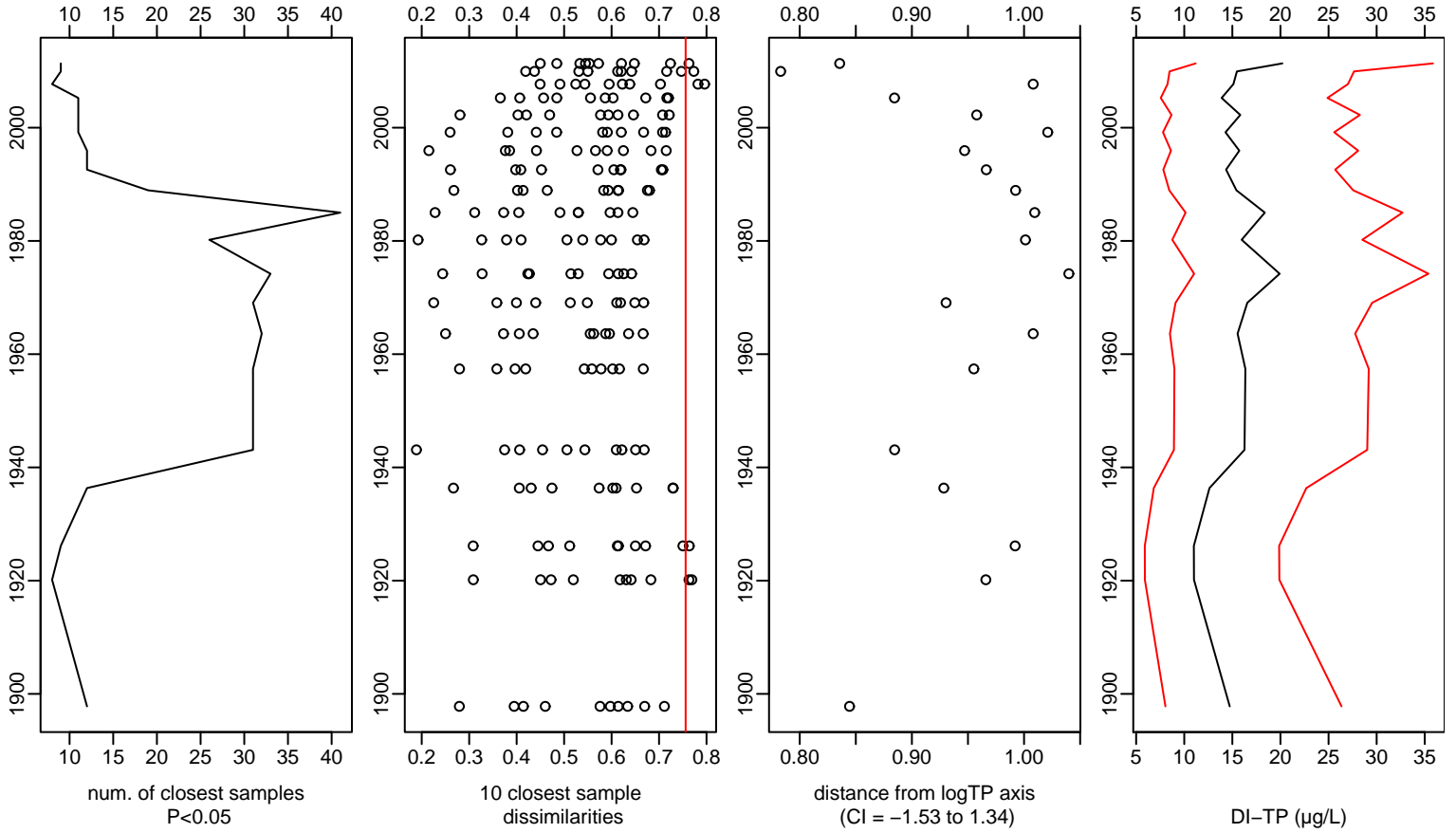
Fig. 12



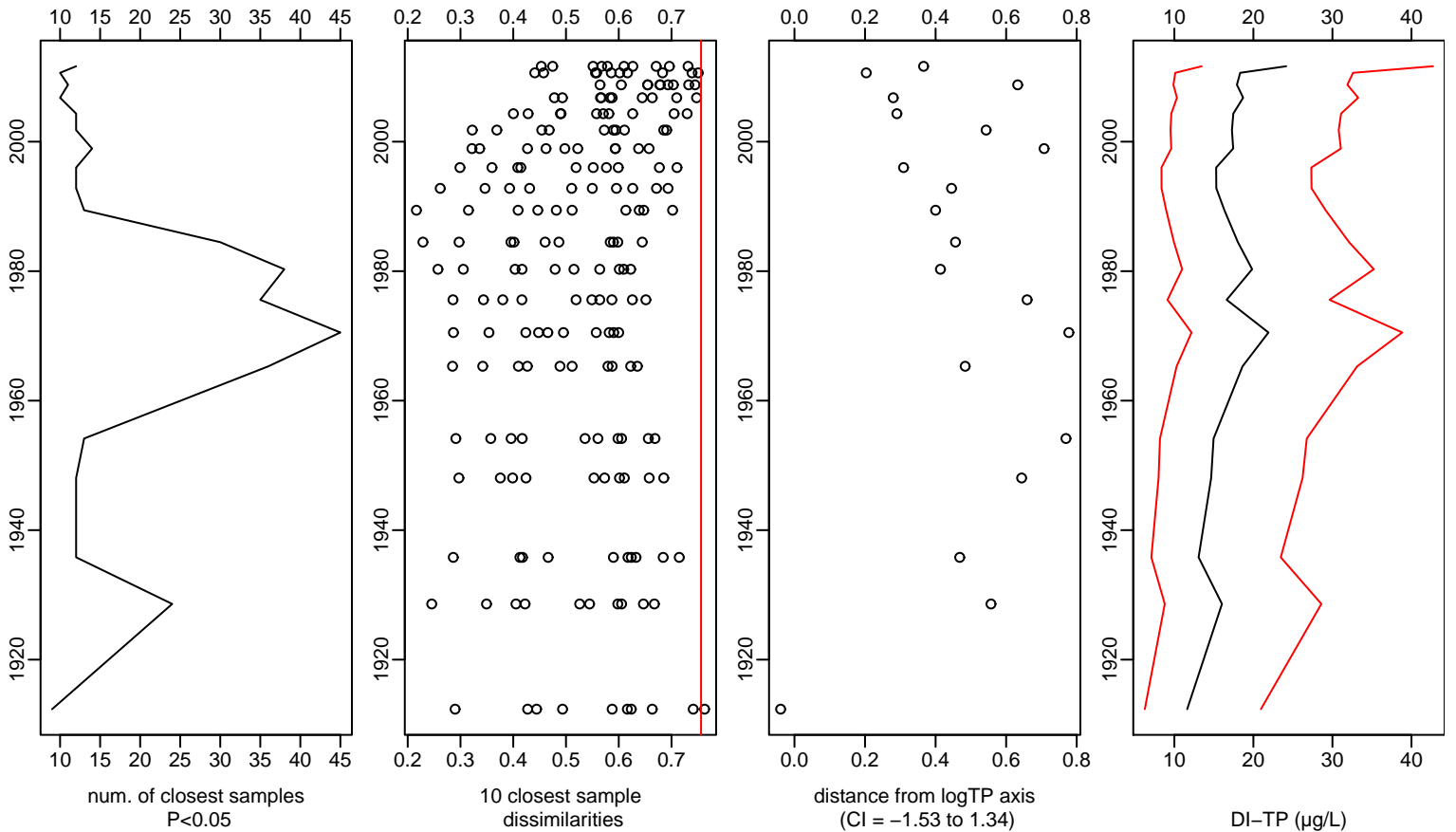
Appendix A.

Diatom assemblage analog, fit-to-TP and DI-TP results for seven sediment cores from Lake of the Woods. From left to right stratigraphic plots indicate: (1) the number of significantly close modern phytoplankton sample assemblages to each fossil assemblage based on analog analysis; (2) dissimilarity values for the 10 modern assemblages closest to each fossil assemblage (red line indicates 95th percentile based on all modern samples); (3) distance of each fossil sample from the TP axis in a CCA constrained to TP (lower and upper extremes of the 95% confidence interval shown in axis label); (4) DI-TP for fossil assemblages (black line indicates inferred TP and red lines indicate the range of model error).

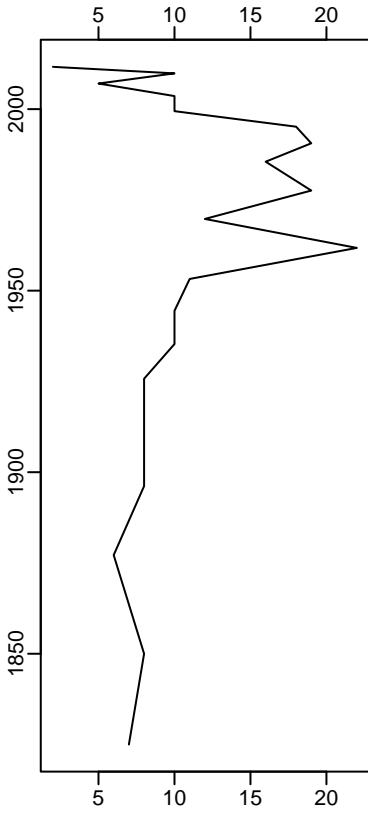
Big Traverse 3



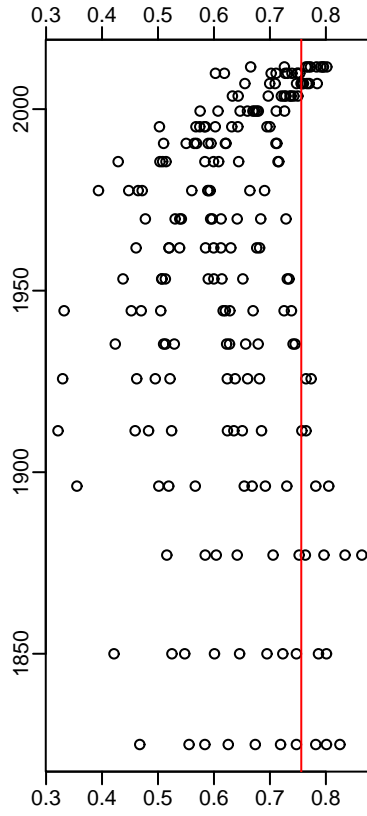
Big Traverse 4



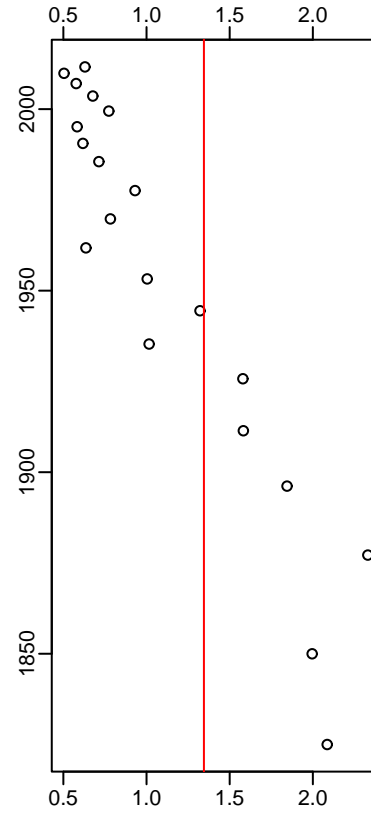
Muskeg



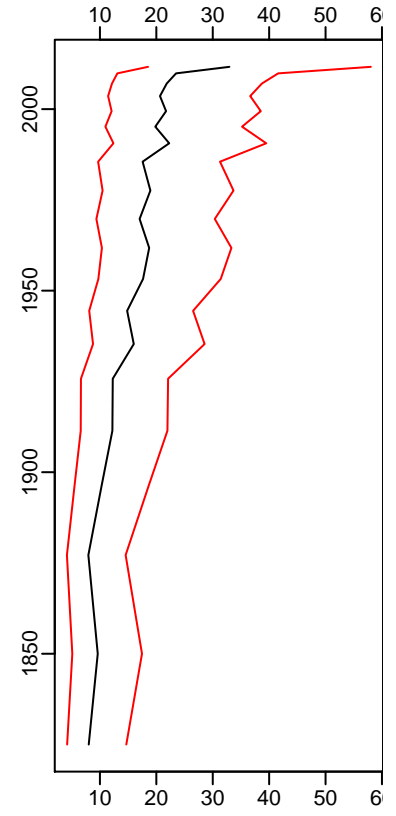
num. of closest samples
 $P < 0.05$



10 closest sample
dissimilarities

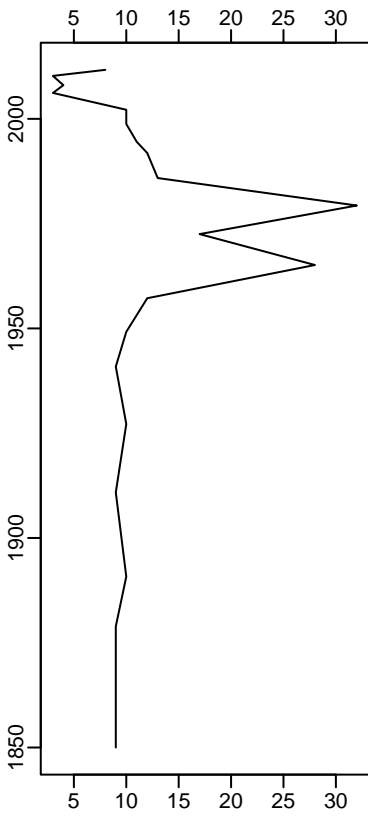


distance from logTP axis
(CI = -1.53 to 1.34)

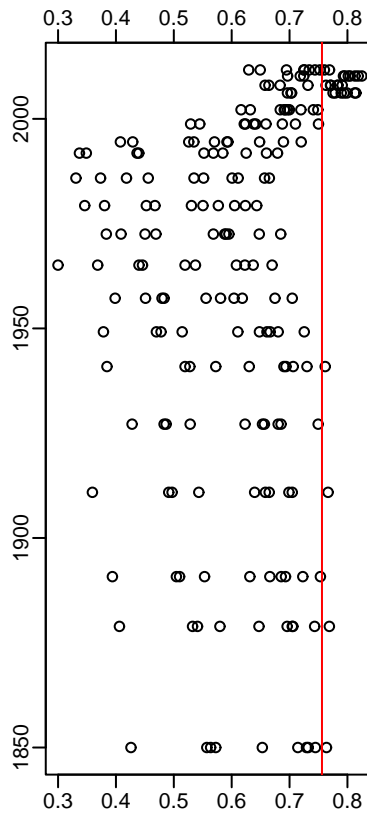


DI-TP ($\mu\text{g/L}$)

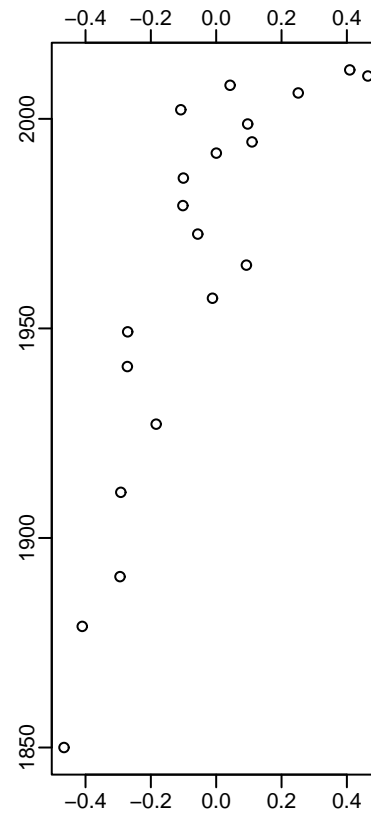
Sabaskong



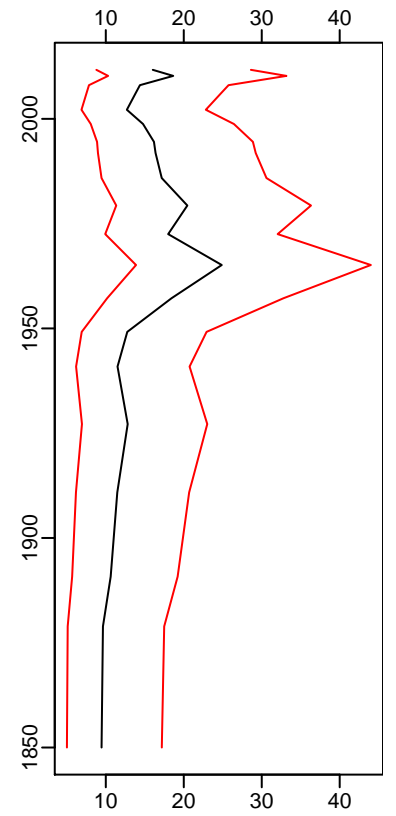
num. of closest samples
 $P < 0.05$



10 closest sample
dissimilarities

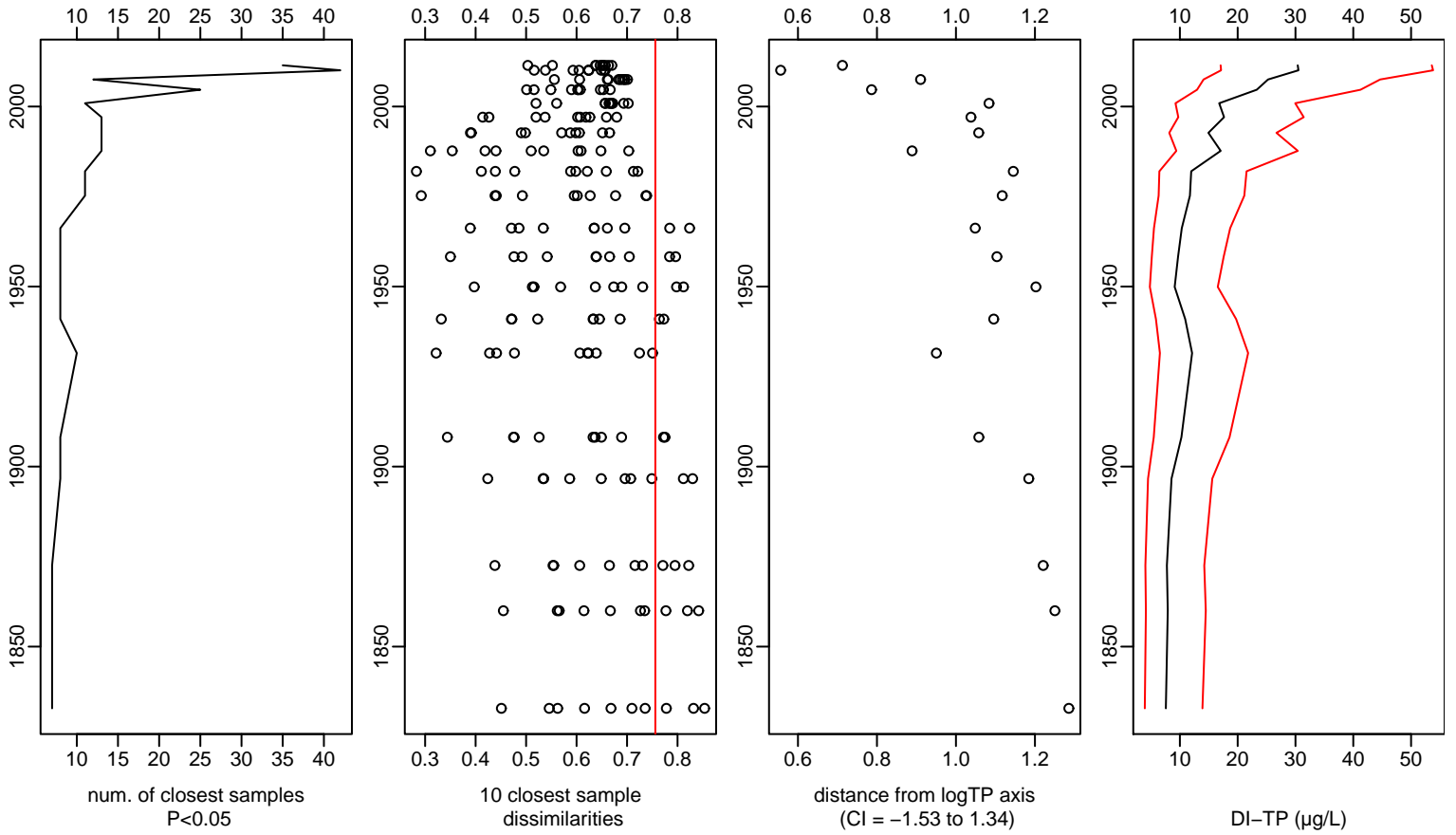


distance from logTP axis
(CI = -1.53 to 1.34)

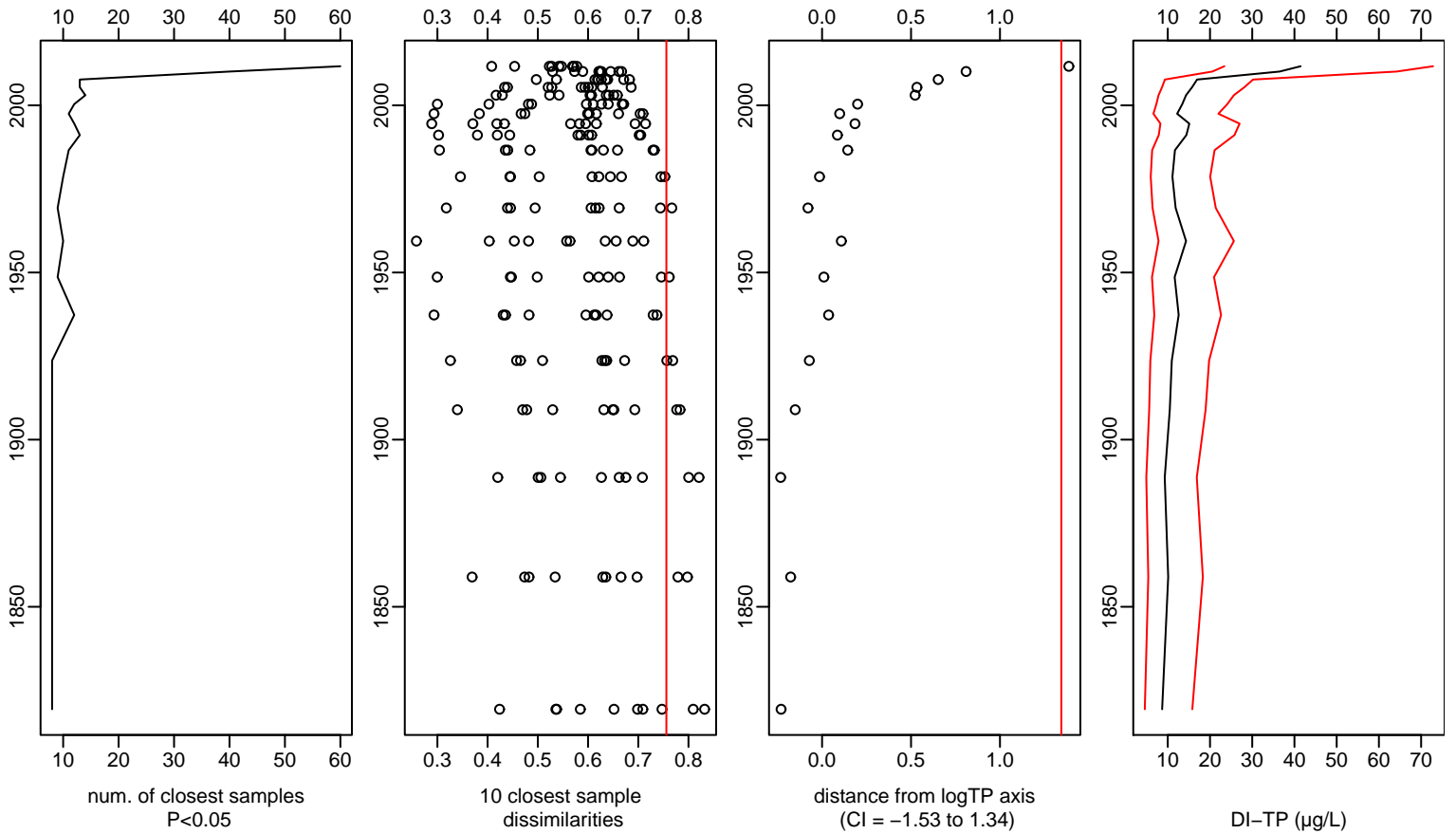


DI-TP ($\mu\text{g/L}$)

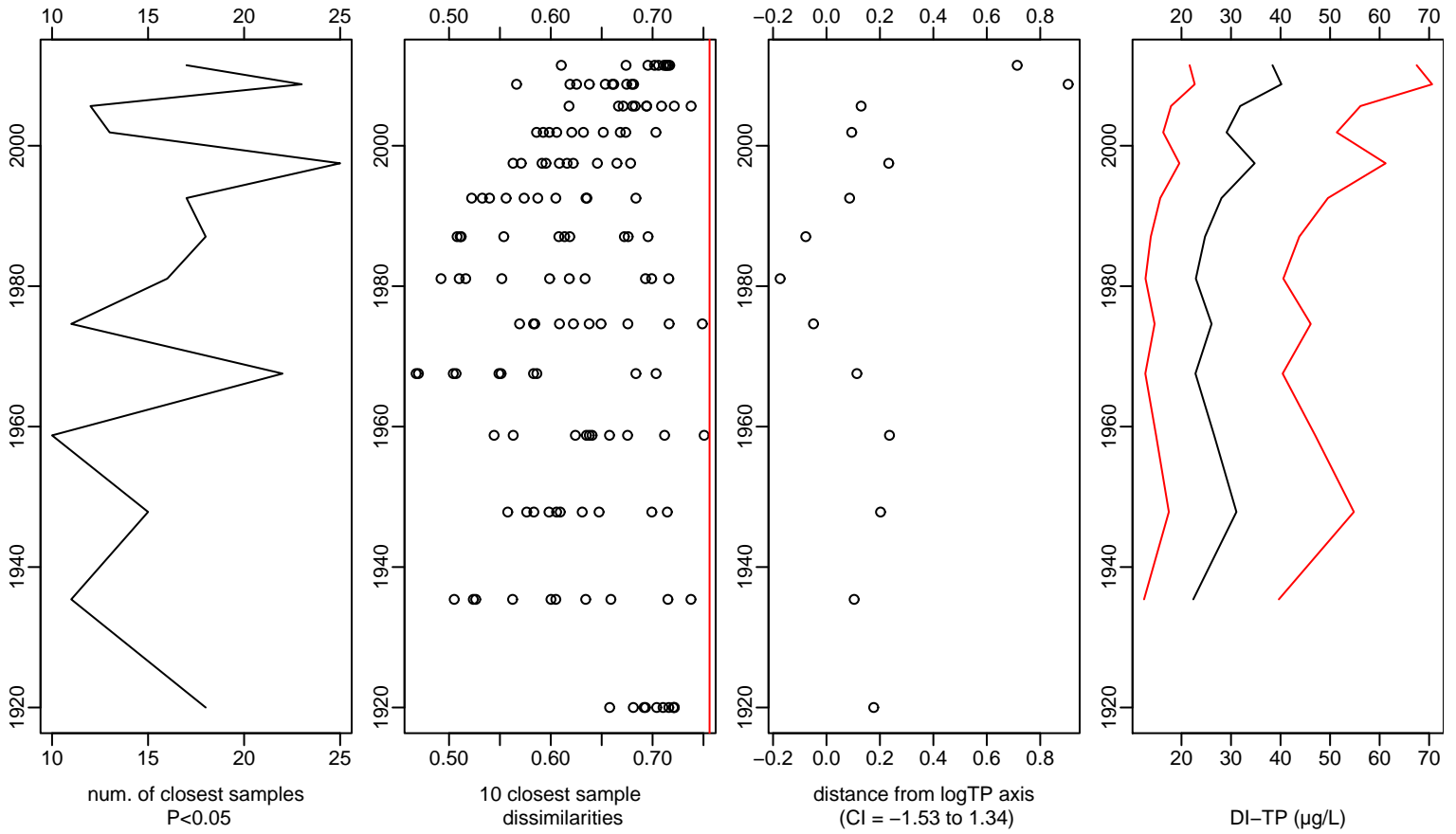
Little Traverse



Big Narrows



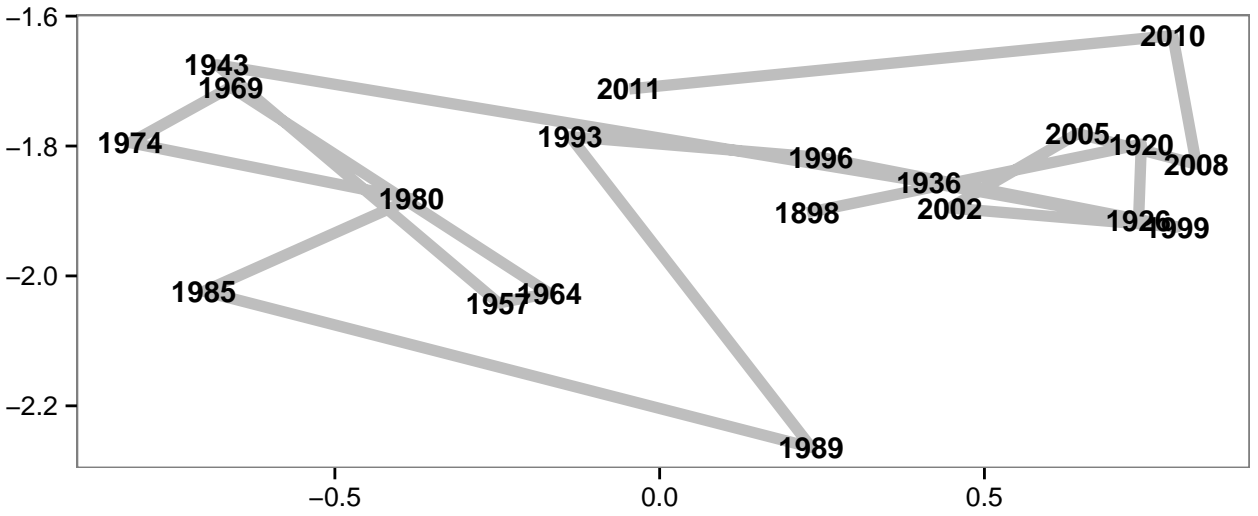
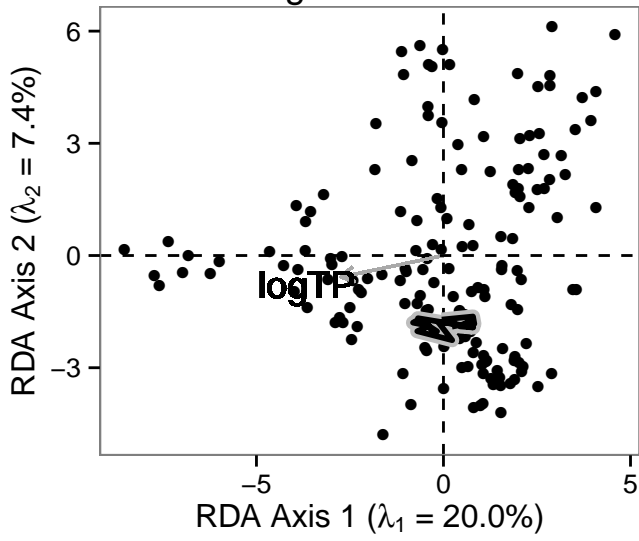
Buffalo



Appendix B.

Tracking of fossil diatom assemblages relative to the diatom-based model assemblages, including an evaluation of the appropriateness of downcore inferences DI-TP. From top to bottom plots indicate: (1) A redundancy analysis of model assemblages (black circles) constrained to measured environmental data (log-transformed TP vector shown), including passive ordination of the fossil assemblages (black line with gray outline); (2) A zoomed-in track of the fossil assemblages, indicating the dates associated with each fossil assemblage; (3) A plot of DI-TP regressed against axis one scores of a principal components analysis of the fossil diatom assemblages. Correlation coefficients with an asterisk (*) are significant ($P < 0.05$).

Big Traverse 3



Big Traverse 3 $r = -0.15$

