FRESHWATER

NONYLPHENOL & SEDIMENTATION HISTORY
IN RIVERINE LAKES

Twin Cities Metropolitan Area, Minnesota

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Executive Summary

This study was designed to investigate the occurrence in the environment of a class of compounds, Nonylphenol (NP) and many nonylphenol ethoxylates (NPEs) that have been used since the 1940s as detergents and surfactants, among other things. They are known endocrine disruptors and can be produced in wastewater treatment plants. The goal was to document the current concentrations of NP and NPEs within the Twin Cities' metropolitan watershed and assess how they have changed over time.

Though the Environmental Pollution Agency (EPA) now requires notification of significant new uses so that a risk assessment can be performed before commercial production begins, the state of Minnesota has yet to issue regulatory recommendations or implement water quality standards for the pollutants. As a result, the contaminants are still in commercial use and continue to be produced as a byproduct in wastewater treatment effluent.

Lake sediment is a potential archive for these compounds because they sorb to sediment. Four floodplain lakes in the Twin Cities metropolitan area located both up- and downstream of the wastewater treatment plants were selected to determine the spatial and temporal distribution of the compound. Cores were taken so that they could be sampled for compounds in the time spanning 1940 to present with one pre-1940 sample for control.

A depth-age model for each core had to be constructed in order to sample at the appropriate depth. Changes in pollen abundance in lake sediment were used to build a timeline for sediment accumulation. Major ecological shifts indicated by pollen assemblage were correlated to cores with horizons dated with one of two radiometric methods to develop a depth-age model. This resulted in an update of the sedimentation rates in the floodplain lakes and Lake Pepin.

Although the compounds were detected in the cores, detection limits and pandemic delays interfered with the results, leaving questions about the actual distribution and abundance. The compounds are present at levels near the detection limit that we achieved, but that can be improved upon. The methodology deployed to retrieve and sample the cores is robust and the compounds deserve a more thorough investigation.

Revised sedimentation rates for the periods 1855-1974 and 1974-2019 for the floodplain lakes show 1.7, 3 and 3.5 fold increase in the sedimentation rates in the post-1974 period for Rice, Pig's Eye and River lakes, respectively. Lake Pepin continues to accumulate sediment at the previously reported rates or slightly lower, both still an order of magnitude higher than pre-settlement rates.

Introduction

Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) are nonionic surfactants within the larger group of Alkylphenol Ethoxylates (APEOs) (Ying et al., 2002; White et al., 1994). The structure of these chemicals is comprised of a polar (hydrophilic) alkylphenol ring and a nonpolar (hydrophobic) ethoxylate chain (Ying et al., 2002). This amphiphilic structure allows the compounds to form micelles when in solution and reduce solution surface tension (Thiele et al., 1997). These functions enable the chemicals to be employed as dispersing, emulsifying, floating, and cleaning agents in industrial and household applications (Thiele et al., 1997). As a result of APEOs being most commonly used in solution, they are frequently discharged into municipal and industrial wastewater and then transferred to wastewater treatment plants (WWTPs) (Acir, 2018). Throughout the wastewater treatment process, microorganisms are introduced into the water which can biodegrade APEOs into multiple products including (4-alkylphenoxy) acetic acid (AP1EC), (4-alkylphenoxy) ethoxy acetic acid (AP2EC), 4-alkylphenol monoethoxylate (AP1EO), 4-alkylphenol diethoxylate (AP2EO), and 4-alkylphenols which include NPE and Octylphenol ethoxylates (OPE) (Acir et al., 2018; Thiele et al., 1997). Most commonly, these byproducts are then discharged directly into major waterways.

The endocrine system in organisms regulates their reproductive, physiological, and developmental functions. This is accomplished through the release of cell signaling chemicals, called hormones, which are received by hormone receptors and trigger a cellular response. Endocrine disruptors (ED) are synthetic compounds that have a similar chemical shape to natural hormones and can alter normal endocrine expression (Matthiessen et al., 1998). APOEs have been established as endocrine disrupting compounds. The daughter degradants with shorter chains, such as NP and NPE, have been found to be the most endocrine active (Jobling et al., 1994; Lye et al., 1999; Gabriel et al., 2008). Most APEOs are 17β-oestradiol mimics; these structures are particularly harmful for developing organisms and can lead to alterations in liver function, testicular growth, and even male feminization (Jobling et al., 1996; Uguz et al., 2003; Hsu et al., 2016; Servos et al., 1999). NPE is also bioaccumulative and toxic to aquatic organisms (Ahel et al., 1992; Uguz et al., 2003; Burkhardt-Holm et al., 2000; Hughes et al., 2000). However, different NPE isomers do have varying levels of endocrine activity and toxicity, making it difficult to make generalized statements for the entire family of chemicals (Uchiyama, 2008; Preuss, 2006).

There is significantly less published information on the effects of APEOs on human health. There is global evidence of the APOE presence in vegetables, meats, and bottled drinking water (Lu et al., 2013; Shao et al., 2007;

Loyo-Rosales et al., 2004). A German study calculated that the average German adult ingests 7.5 µg/day of NPE and infants can ingest 1.5 µg /day of NPE if fed on infant formula (Guenther et al., 2002). The largest concern of APOEs is its impact on human fetal development as well as its potential impact on nervous system function and immunoregulatory processes (Hu et al., 2014; Patiño-García et al., 2017; Lee et al., 2003; Sato et al., 2002). It is believed the health impacts of APEOs can occur even in small doses, but more research is needed to make definitive statements about their impacts (Neubert et al., 1997; Kavlock et al., 1996; Hu et al., 2014).

Global response to APOE use has been inconsistent. While many European countries have implemented environmental quality standards of 1µg/L for most APOEs, and the Association of Asian Southeast Nations (ASEAN) has taken similar steps to Europe, the United States does not have any environmental quality standards in place (Acir et al., 2018; Renner, 1997). As of 2014, the U.S. EPA has added 15 NP/NPE chemicals to its Significant New Use Rule (SNUR), which enables the EPA to conduct a review of any new or resumed use of the chemicals on the list. If determined appropriate, the EPA is then allowed to limit or prohibit the implementation of these chemicals before they are put into production (US EPA, 2020).

NPOE does not persist long in water with photochemical degradation half-lives are between 10 and 15 hours and aerobic degradation half-lives are between two and seven days (Ahel et al., 1994; Ying et al., 2002). However, as a result of the compound's low K_{ow}, it readily sorbs to sediments and has an anaerobic half-life of up to 60 years (Soares et al., 2008; Mao et al., 2012; Thiele et al., 1997). Because of this, previous paleolimnological studies focusing on APEOs have been conducted and contaminant chronologies have been successfully constructed (Macromini et al., 2009; Shang et al., 1999; Isobe et al., 2001).

PREVIOUS WORK IN MINNESOTA

The state of Minnesota also does not have an environmental quality standard for APOEs and cites the lack of established EPA analytical methods as well as low testing concentrations throughout the state in 2010 (Biewen, 2018; Monson, 2010). In Minnesota, APEOs have been detected up- and downstream of WWTPs as well as within their effluent (Lee et al., 2004; Lee et al., 2008). Additionally, vitellogenin, a key indicating protein of endocrine activity, was found in 57 % of the 415 male fish sampled in the study (Lee et al., 2008).

It is unclear how prevalent these contaminants are within Minnesota waterways, what the current concentrations are, and how they have changed over time, particularly within the last 20 years when their use was discouraged. Judy Crane of the MPCA, who holds a doctorate in water chemistry, has studied the distribution of alkylphenols and nonylphenol ethoxylates across Minnesota by sampling shallow lake sediment (0–5 cm sediment depth) and analyzing those samples using high-resolution gas chromatography coupled to a low-resolution mass spectrometer (Fig. 1). She and her team concluded that their presence in the environment in Minnesota was consistent with the degradation of nonylphenol ethoxylates (Crane, 2019).

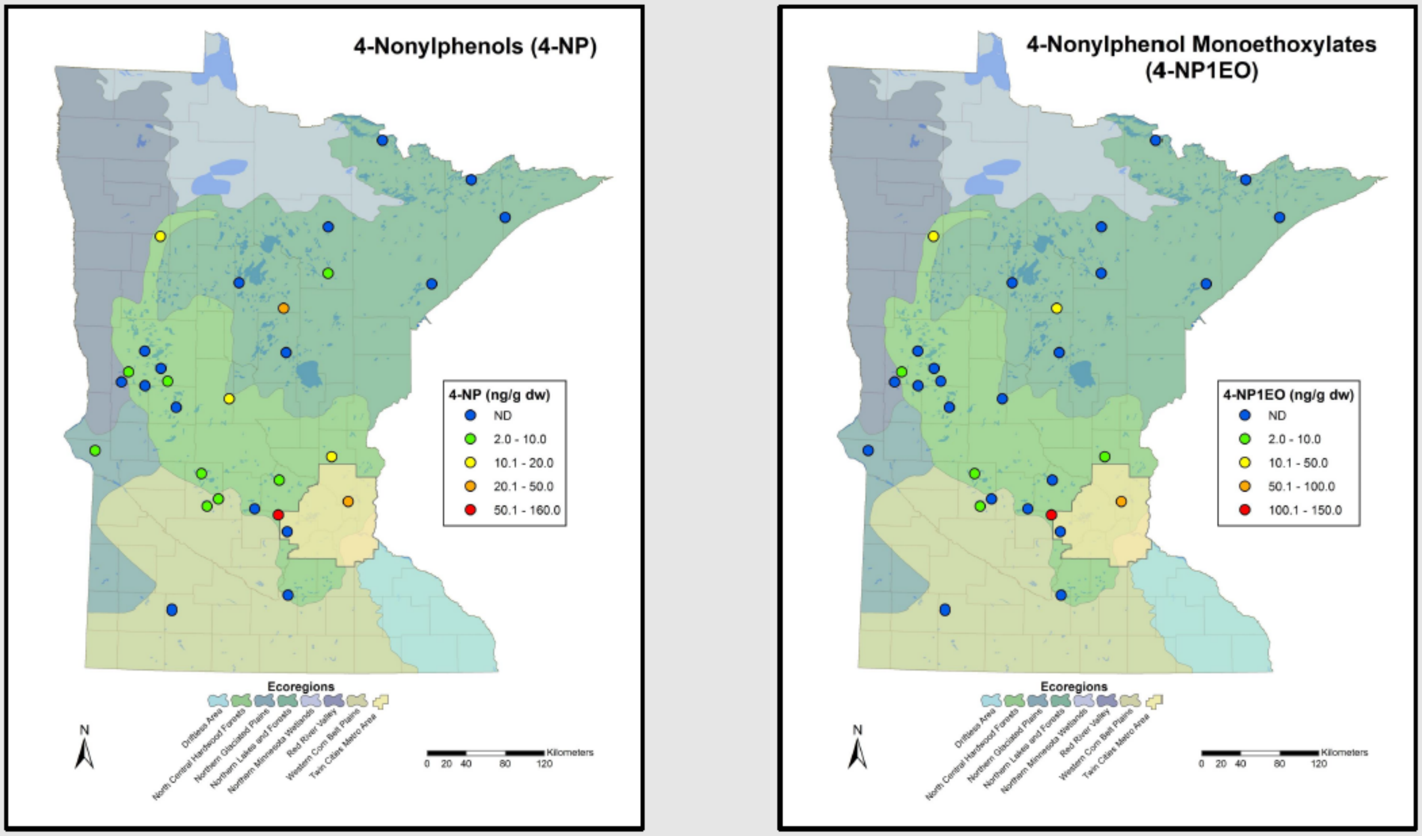


Fig. 1 Previous study results for nonylphenols in lake sediment (0–5 cm). Reproduced from Crane et al., 2018

Project Goals

This study will focus on determining NP and NPE contaminant concentrations in Minnesota starting in 1880, the beginning of European settlement, up to today. There are two overarching goals with a third ancillary goal. The first is to understand the spatial distribution of NP and NPEs throughout the Twin Cities urban watershed by sampling four lakes adjacent to the Minnesota and Mississippi rivers located upstream and downstream of two major WWTPs. The second is to assess the temporal distribution of NP and NPE to assess the effectiveness of the EPA's SNUR and their recommendations for alternative chemicals to be used.

An ancillary goal emerged from the need to construct a robust record of the contaminant in the environment. Lake sediment is an archive of land use, climate change, erosion, sedimentation, vegetation, fire (charcoal), development, and even use of chemical compounds that persist in the environment. An absolute chronology of events is achieved by dating specific sediment horizons and correlating them between cores. Sediment enters a riverine or floodplain lake during flood events and by way of its tributaries; some may be airborne. Pollen is commonly airborne and changes in pollen assemblage over time represents ecological shifts in the surrounding landscape that can be linked to discrete time periods. Variations in mineral properties of the sediment like magnetic properties can indicate a change in sediment source. All of these records help constrain the core history.

Sampling for pollen analysis to determine the proper time periods for chemical sampling took place in the winter of 2019-20. A pollen stratigraphy and depth-age model was needed before chemical samples could be taken. We cored one additional lake, Lake Pepin, for the purposes of correlating and updating those sedimentation records. This is helpful for watershed districts, landholders and conservation districts who have been implementing or recommending practices to reduce sediment loading to determine their impact.

Methods

In order to receive a comprehensive understanding of NP and NPE distribution throughout a majority of the southern

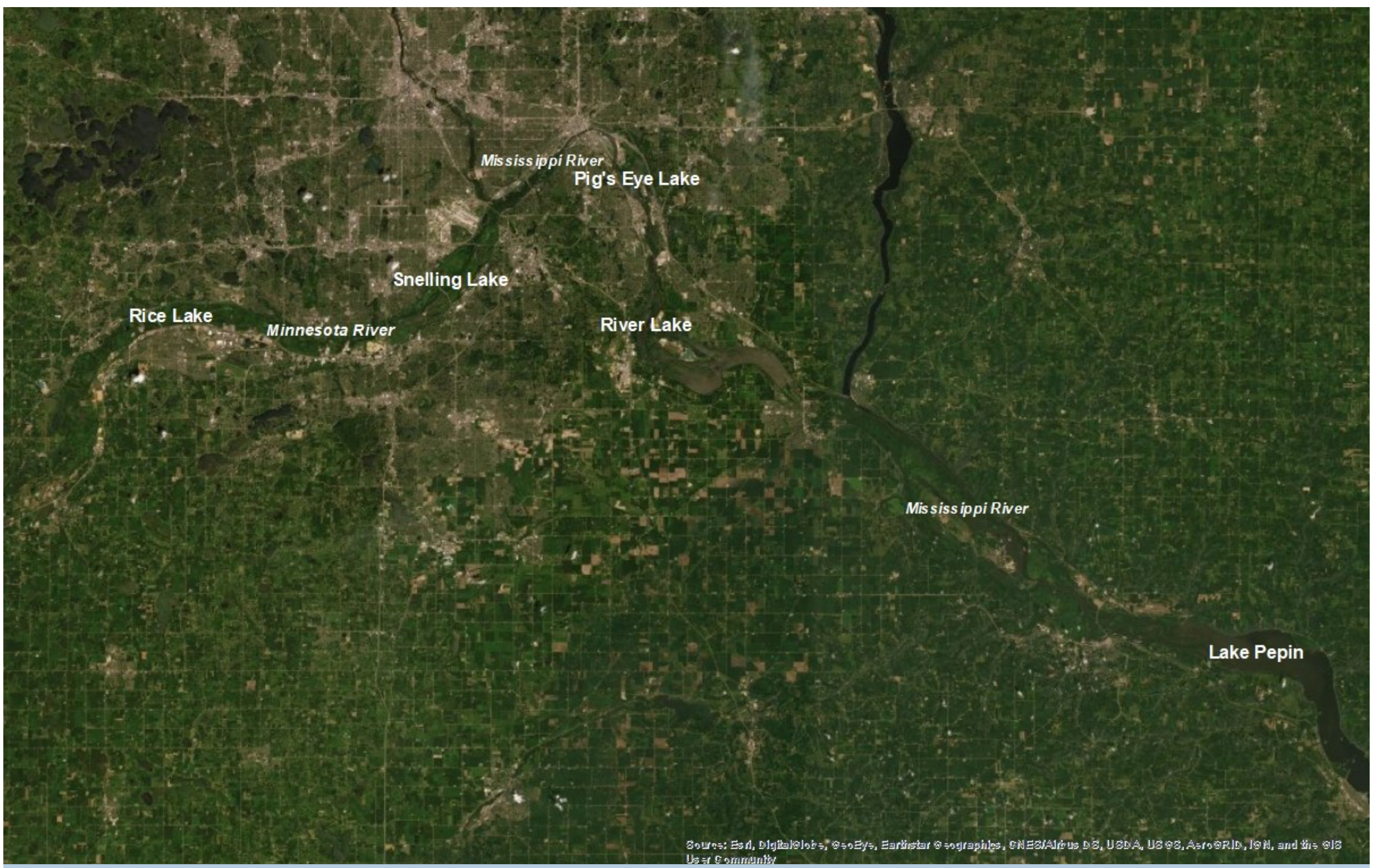


Fig. 2 Locations of lakes cored along the Minnesota and Mississippi rivers

Twin Cities metropolitan area, four lakes adjacent to the Minnesota and Mississippi rivers were selected (Fig. 2). Lakes were chosen based on their position relative to major wastewater treatment plants (WWTPs) within the area. Rice Lake (UTM 15T E 459236.11, N 4962410.65) is the easternmost lake sampled and is adjacent to the Minnesota River. It was considered upstream of many of the major WWTPs in the area. Then, moving east on the Minnesota River, the next lake was Snelling (UTM 15T E 485238.51, N 4969653.71), which is downstream from the Blue Lake WWTP and the Seneca WWTP. Pig's Eye Lake (UTM 15T E 497757.03, N 4973608.75) is adjacent to the Mississippi river and immediately downstream of the Metro Plant WWTP in St. Paul. River Lake (UTM 15T E 498592.42, N 4961644.36) is positioned much farther downstream of Metro Plant WWTP. Finally, Lake Pepin (UTM 15T E X, N X) touches both the Minnesota and Wisconsin borders and is also the southernmost end of the Mississippi River within Minnesota. All of these lakes are on the floodplains of the Minnesota and Mississippi rivers or on the river itself and are subject to periodic inundation by floodwater. They receive much of their sediment during high water events, with the rest being delivered by tributaries streams or created within the basin biogenically. We took a transect of cores in each lake to look for sediment focal points and compare cores to look for discontinuities in the sediment and pollen stratigraphy. We also used archived cores formerly taken in the area for correlation purposes.

FIELD METHODS

Lac Core staff Mark Shapley, Ph.D., Vania Stefanova, Ph.D., and Kristina Brady helped organize and assisted with coring field work using a modified Livingstone corer deployed from a floating platform created by lashing two canoes together. Anchors for the platform were set by a person in a third canoe. (Fig. 3).

A new core was taken in Rice Lake near a previous coring location (Jennings et al., 2019) to get a fresh sample for chemical analysis. One1.6 m drive was recovered so that pollen and sediment could also be correlated to the earlier core. Access to this lake required a permit from the U.S. Fish and Wildlife Service and permission from Hennepin County to travel on a road under construction.

Fig. 3. Canoes lashed together will drill rods form the portable coring platform

Snelling Lake had also been previously cored (Blumentritt, 2013). This lake has a mean sedimentation rate of 2.5 mm/year or 0.085 g/cm^2/year rate based on the Pb-210 dating of the core (unpublished data). Access to this lake required a DNR permit and because the park was closed due to flood damage, special permission was required and DNR staff accompanied us during the coring (Fig. 4). One1.6 m drive was planned to allow

Fig. 4 Coring Snelling Lake in Fort Snelling State Park

correlation to the existing core which had been dated but had no pollen analysis. A pollen stratigraphy was planned for the new and old cores for correlation purposes so that Pb-210 dating could be applied across the cores.

Pig's Eye Lake was accessed from a landing in South St. Paul, which required paddling across the Mississippi River. After reaching the lake, the canoes were lashed together to create a platform. A transect of cores was taken to determine the focal point for sediment and best location for analysis. After review, a single core was selected for having the most complete record for sediment description, chemical analysis, and dating. The history of manipulation of the landfill may factor into the preservation of the sediment record in this lake. We only analyzed for our selected chemicals, but odors and colors in this core suggested a more thorough study of contaminants may be in order.

River Lake had been previously cored for a study by a Macalester College class and supervised by Joy Ramstack, who is a St. Croix Watershed Research Station employee. She and the faculty advisor provided records and recollections. A transect of cores was taken to determine the sediment focal point, as this appeared to be the most connected to the river, even at low flows.

Lake Pepin was re-cored as close to three previous sites as possible using a boat and staff provided by the St. Croix Watershed Research Station.

Core Site	1995/96		2019		Distance
	LatDD	LonDD	LatDD	LonDD	Difference (m)
II.3	44.54439	92.32118	44.54443	92.32114	5.2
III.2	44.49837	92.30531	44.49842	92.30533	5.8
IV.2	44.44915	92.24636	44.44917	92.24638	2.7

Table 1 GPS coordinates for the two sets of cores. The original GPS readings were derived with real-time differential correction, which was necessary back in 1995/96 because the military degraded the satellite signals.

CORE PROCESSING

Cores processing took place at the Lac Core facilities in Tate Hall at the University of Minnesota Department of Earth and Environmental Sciences in Minneapolis. The lab's standard initial core description procedures include both written and photographic documentation, whole-core logging with an automated sensor, and detailed visual description of sedimentology and sedimentary structures, mineralogy, and biological components (http://lrc.geo.umn.edu/laccore/assets/pdf/sops/icd.pdf, accessed June 29, 2021). Those results are included in the appendices of the digital version of this report or are archived at Lac Core and Freshwater depending on table and file size.

All cores were scanned while intact at least every 5 mm for their physical properties (p-wave velocity, gamma-ray-density and magnetic susceptibility) using a GEOTEK™ multi-sensor core logger. Cores were then split using a series of tools to first cut through the casing (Fig. 5), then the sediment, and finally to clean the sediment face for photographing and description.

Loss on Ignition (LOI)

Organic matter in cores collected in these settings may include algal matter produced within the lake itself, local vegetation from lake margins and the surrounding floodplain, and the organic component of sediment transported down the Minnesota River. Carbonate mineral sediment includes both a carbonate component of the Minnesota River sediment load derived from carbonate-bearing sedimentary rocks, and carbonate sediment produced through biochemical precipitation within the lakes. Noncarbonate mineral matter may include locally eroded silt and sand from the immediate watershed, but in these settings will be primarily derived from upstream erosion in the watershed of the Minnesota River and its tributaries.

Fig. 5 Amy Myrbo, Ph.D. and Rob McManus splitting core tube with a vibrating medical cast saw during a training workshop.

Weighed subsamples were taken from regular intervals throughout the cores for loss-on-ignition (LOI) analysis to determine bulk density and dry weight percent of organic, carbonate, and noncarbonate mineral matter. This involved heating sediment subsamples to 105°C to determine dry density, then sequentially heating them at 550°C and 1000°C to determine organic matter and carbonate mineral content from post-ignition weight loss, respectively. LOI sampling was performed by Rob McManus and analysis by LacCore staff.

Magnetic Susceptibility

The bulk sediment measurements of magnetic susceptibility (MS) reflect the concentration of magnetizable mineral phases in the sediment, often viewed as reflecting the concentration of clastic mineral material and interpreted as a signal of erosional intensity on the sediment-contributing landscape. Therefore, magnetic susceptibility can help differentiate sediment input to a lake derived from soil erosion from the organic sediment created in the lake. The magnetic signature of the Pepin cores has been used as a correlation tool and is used again here to update the sedimentation record for the lake (Blumentritt et al., 2013; Engstrom et al., 2009; Blumentritt and Lascu, 2015) and infer flood frequency in Rice Lake.

Pollen

A reference core for each lake was selected for detailed pollen analysis with samples taken at approximately 10 cm intervals. Pollen preparation followed the classical chemical methods including acetolysis (Faegri and Iversen, 1989). At least 200 to 300 terrestrial pollen grains were identified to the lowest possible taxonomic level with pollen keys of Reille (1992; 1998), Beug (2004), and the reference collection housed at the University of Minnesota. Pollen abundance is reported in terms of its percentage of the sum of arboreal pollen, including trees and shrubs (AP,) and non-arboreal pollen (NAP) (excluding pollen types that are known to be overrepresented). Charcoal particles larger than 20 µm interpreted as an indicator of regional fires (Tinner and Hu, 2003) were also counted. Non-pollen palynomorphs were identified according to van Geel and others (1989). Both charcoal and non-pollen palynomorphs are presented as percentages of the main pollen sum. Analysis of the data relied on a program called ***Tilia*** 1.5.11 (Grimm, 2011) that calculated the percentages and created the graphics reproduced here. Pollen sample preparation and counting was done by Vania Stefanova, Ph.D., who also researched the local settlement and vegetation history to provide the ecological framework for interpretation (Fig. 6).

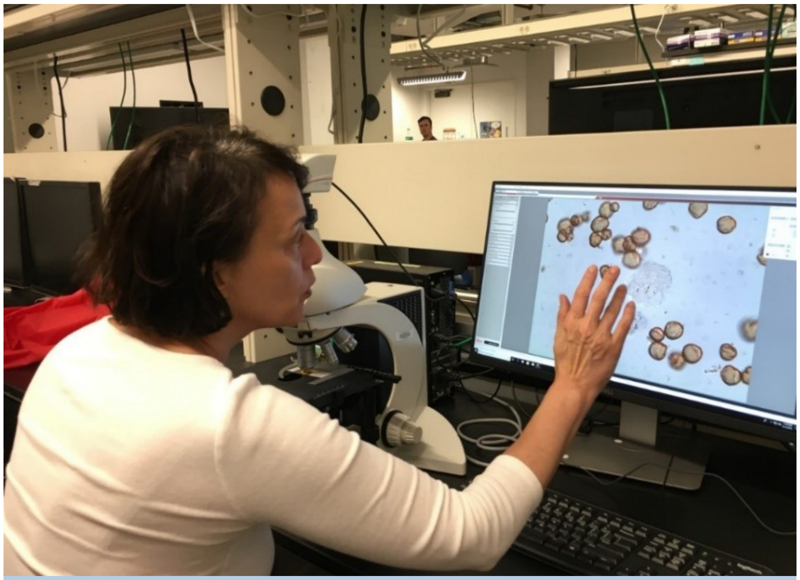


Fig. 6 Pollen preparation and counting were done by Vania Stefanova at the Lac Core lab, Tate Hall, University of Minnesota Twin Cities campus. Here she is displaying the microscopic pollen grains at high magnification for a coring workshop.

RADIOMETRIC DATING METHODS

Both of the following radiometric dating methods were performed by researchers and lab technicians at the St. Croix Watershed Research Station for this project and on existing cores that were previously dated and used to confirm and extend the work of this project.

Pb-210 Dating

For studies that focus on the last 100–200 years, 210Pb a naturally occurring radioisotope in the 238U-decay series is commonly used. It is stripped from the atmosphere in precipitation and accumulates in lake sediments and wetlands where it decays away with a half-life of 22 years. Cores are sampled from the surface to the depth at which 210Pb is no longer measurable (roughly 5–8 half-lives, so 22 years x 5 or x 8). From the resulting 210Pb profile, dates are calculated using a mathematical model that makes assumptions regarding the accumulation of 210Pb and sediment at the core site (https://www.smm.org/scwrs/facilities/laboratories, accessed June 29, 2021).

Cesium Dating

Lakes like those sampled for this project may have highly variable sedimentation rates owing to flood inundation which would lead to errors in 210Pb dating. The presence of 137Cs provides a marker horizon for the 1963 peak from atmospheric nuclear testing and, in Europe, the 1986 peak from the Chernobyl nuclear accident. If this spike in radioactivity is detected, it can corroborate the 210Pb dating and the pollen stratigraphy.

CHEMICAL ANALYTICAL METHODS

Legend Analytical of St. Paul performed the analytical chemistry based on EPA-recommended procedures (https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NERL&dirEntryId=62194) using ultra-performance liquid chromatography-mass spectrometer/mass spectrometry (UPLC-MS/MS) technology and isotopic standards for 4-NP, 4-NPE along with a C13 labeled 4-NPE. Spikes of known concentration of each analyte were used as a control in both a clean matrix and an additional samples. All compounds had recoveries of between 91 and 121%.

Initial results showed no detectable NP and NPEO-2 and very little NPEO-1 (S. Creekmur, written correspondence, 8/31/2020): there were only four detections above the reporting limits in the samples, all for P-N-nonylphneol monoethoxylate, (in LOWMINN2-PIGS19-3A-1P-1, 31-32cm; LOWMINN2-SNE 19-1A-1P1, 44-45.5cm; LOWMINN2-RIVL19-1A-1P-1, 50-51cm and the LOWMINN2-RLHE19-1A-1P-1, 77-78cm). They achieved reporting levels of between 10 to 100 ppb which is quite low but still about two orders magnitude too high for 4-NP for Minnesota sediments (Fig. 7) (Judy Crane, written correspondence, 9/18/2020 and Crane, 2018).

Legend Analytical agreed to re-extract samples from the remaining sediment and analyze them with a detection limit of 4-NP RL at around 2-5 ng/g or 1 ppb (dry weight). The NPEO-1 results were not able to be lowered (written correspondence, Scott Creekmur, 10/9/2020). Those results are included in Appendix 6.

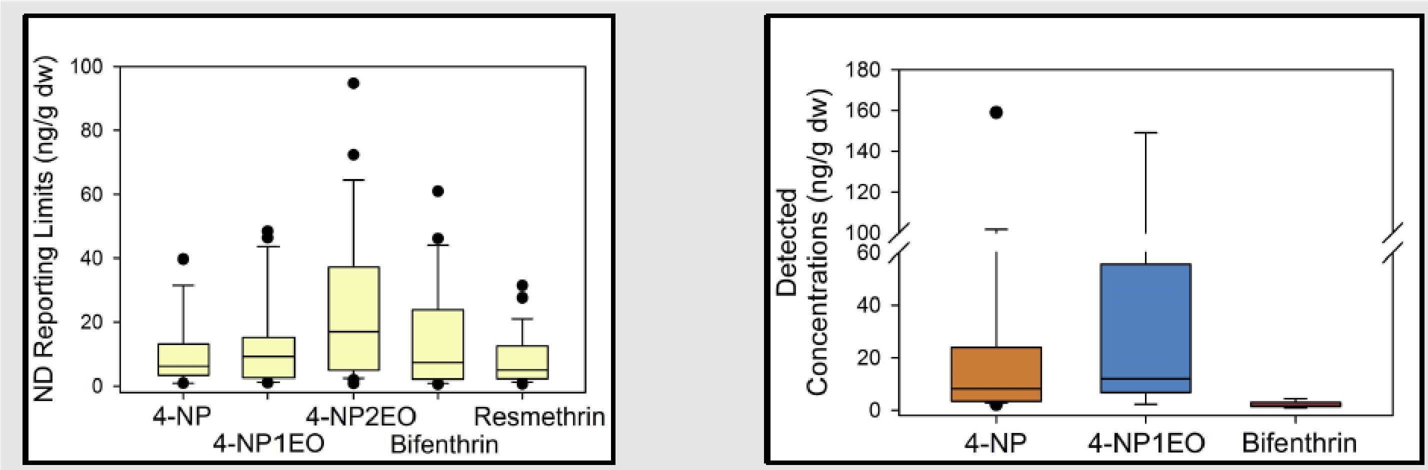


Fig. 7 Reporting limits and Detected Concentrations in nanograms/gram dry weight (1 ppb), reproduced from Crane, J. 2018.

Results

There were no detectable unconformities in the cores from the riverine lakes. Other features were unremarkable with the exception of the magnetic record in Rice Lake, explained below and previously interpreted as recording recent flood events. Photographic images are available for all cores; 11 of them were described by M. Shapley, Ph.D., and are included in Appendix 2.

POLLEN STRATIGRAPHY

The cores selected for detailed pollen analysis were:

- River Lake (LOWMIN2-RIVL19-1A)
- Snelling Lake (LOWMIN2-SNE 19-1A)
- Pig's Eye Lake (LOWMIN2-PIGS19-3A)
- Rice lake (LOWMIN-RC17-1A)

The initial chronology for each of these cores was developed based on correlation of the pollen stratigraphy with a pollen record for a core in Snelling Lake (Fig. 8, SNL 2009) that had been previously dated with ^{210}Pb (unpublished data, D. Engstrom). All of the pollen diagrams have high similarity in the characteristics of the major pollen types and the AP/NAP ratios as shown in the pollen diagrams presented here. The distinctive pollen features used for developing the depth-age models are noted below (Table 2).

Table 2 Depth-age model for SNL 2009, a radiometrically dated core.

Top of Interval (cm)	Date (A.D.)	Notes
0	2009.1	The year of coring
4	2005.8	
10	1999.6	
14	1992.0	
16	1986.7	
20	1974.1	Sharp decrease in elm
24	1957.0	
28	1932.4	
32	1907.8	
36	1886.5	
40	1868.6	
42	1855.5	*Ambrosia* rise associated with Euro-American settlement supported by historical data for Fort Snelling and Shakopee for Rice Lake.
46	1820.7	

Detecting the elm decline in the palynologically studied lakes in this region is a novel and useful finding. Historical data about Dutch elm disease in the Twin Cities metropolitan area shows that by 1977, St. Paul had lost approximately one third of its elms, by 1978 only 30,000 remained, and by 2015, only several hundred trees still stood. Minneapolis lost about half of its elms by 1990 (100,000) (Soll, D., 2016). Therefore, the sharp drop in the elm pollen percentages around 1974 in core SNL 2009 most probably resulted from the wholesale removal of trees infected with Dutch elm disease.

The pollen diagrams for the original core from Snelling Lake (Fig. 8, SNL 2009) and a core taken for this project (Fig. 9, SNEL 2019) also show high similarity in the characteristics of all main pollen types and the AP/NAP ratio. Therefore, the linear depth-age models created in ***Tilia*** (Grimm 1991-2011) for SNL 2009 using the ^{210}Pb dating for control and for SNEL 2019 using pollen stratigraphy are consistent (Fig. 10 A and B). The good agreement between the two depth-age models also suggests that the elm decline at around 1974 is a reliable pollen feature that can be used for pollen-based, depth-age models in this region.

The depth-age model for River Lake (RIVL 2018) based on the coring year, the ***Ambrosia*** rise of 1855, and the elm decrease of 1974 shows a good correlation with the cesium dating for the lake, further supporting the use of the newly recognized elm decline for pollen stratigraphy in this region (Fig. 11).

The same logic is applied to Pig's Eye Lake (Fig. 12).

In the case of Rice Lake (RL-1, 2017), applying the discussed pollen-based model used for the Snelling, River and Pig's Eye lakes, reveals a good correlation between magnetic susceptibility with historic flood records (Fig. 13) (Jennings et al., 2019).

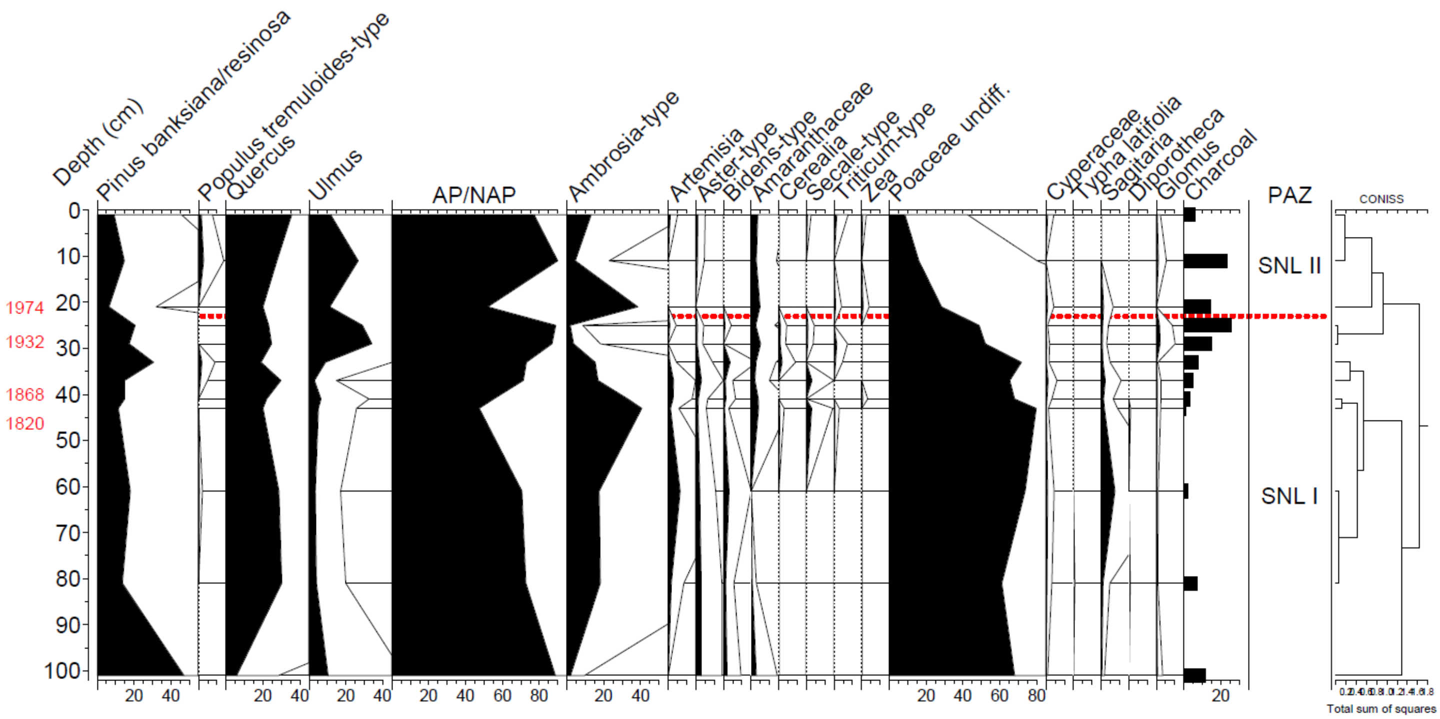


Fig. 8 Snelling Lake, Core SNL 2009. Pollen percentages of the major pollen types

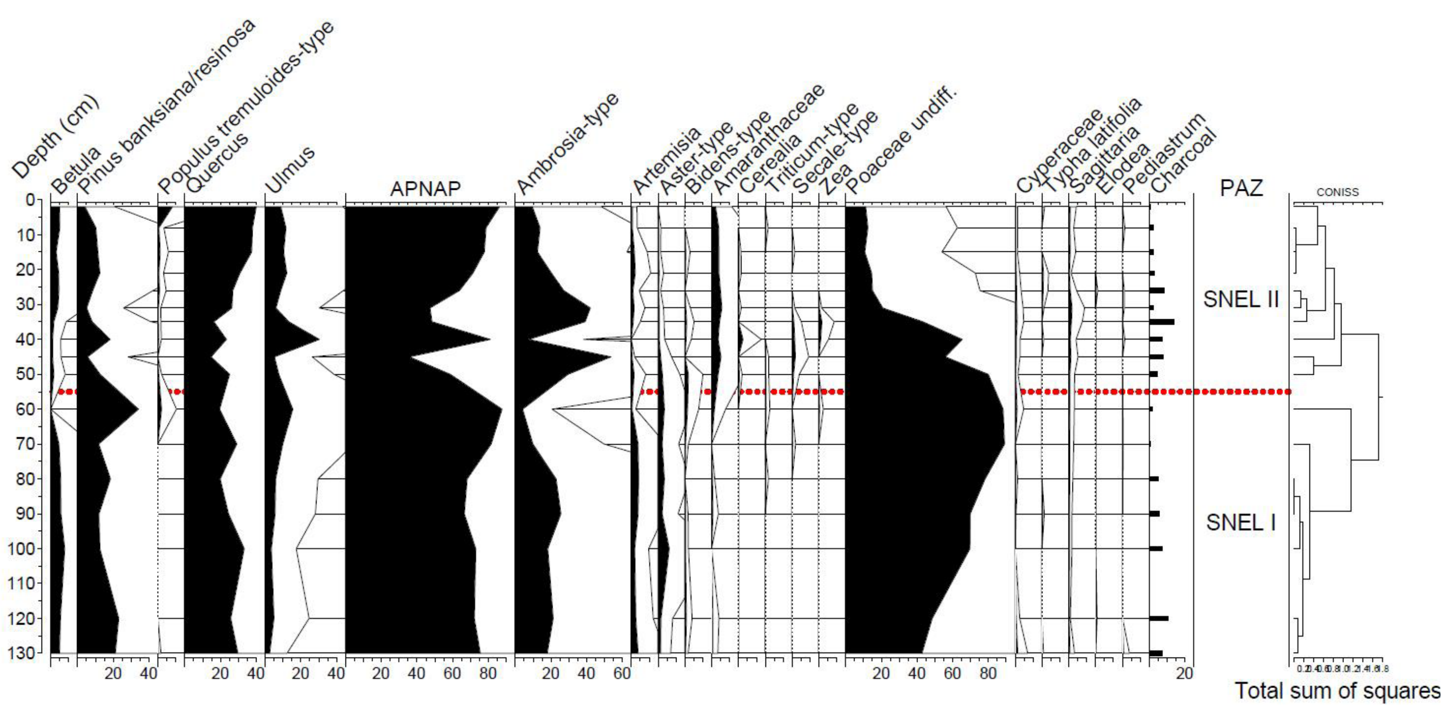
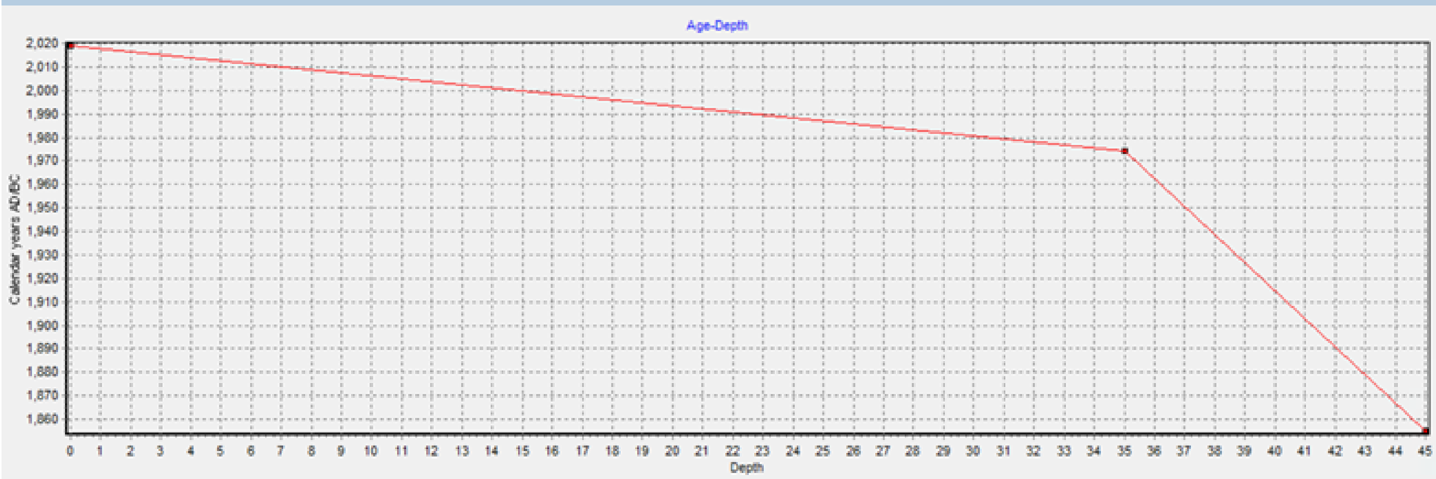


Fig. 9 Snelling Lake, Core LOWMIN2-SNEL19-1A. Pollen percentages of the major pollen types

Fig. 10 Snelling Lake depth-age models (A) based on 210Pb and SNEL 2019 (B) based on pollen correlation



In summary, a comparison of the depth-age models based on pollen using the ***Ambrosia*** rise at 1855 as a mark of European settlement, elm decline around 1974 resulting from Dutch elm disease, and the coring year with those based on ^{210}Pb dating and 137Cs dating are reliable and robust.

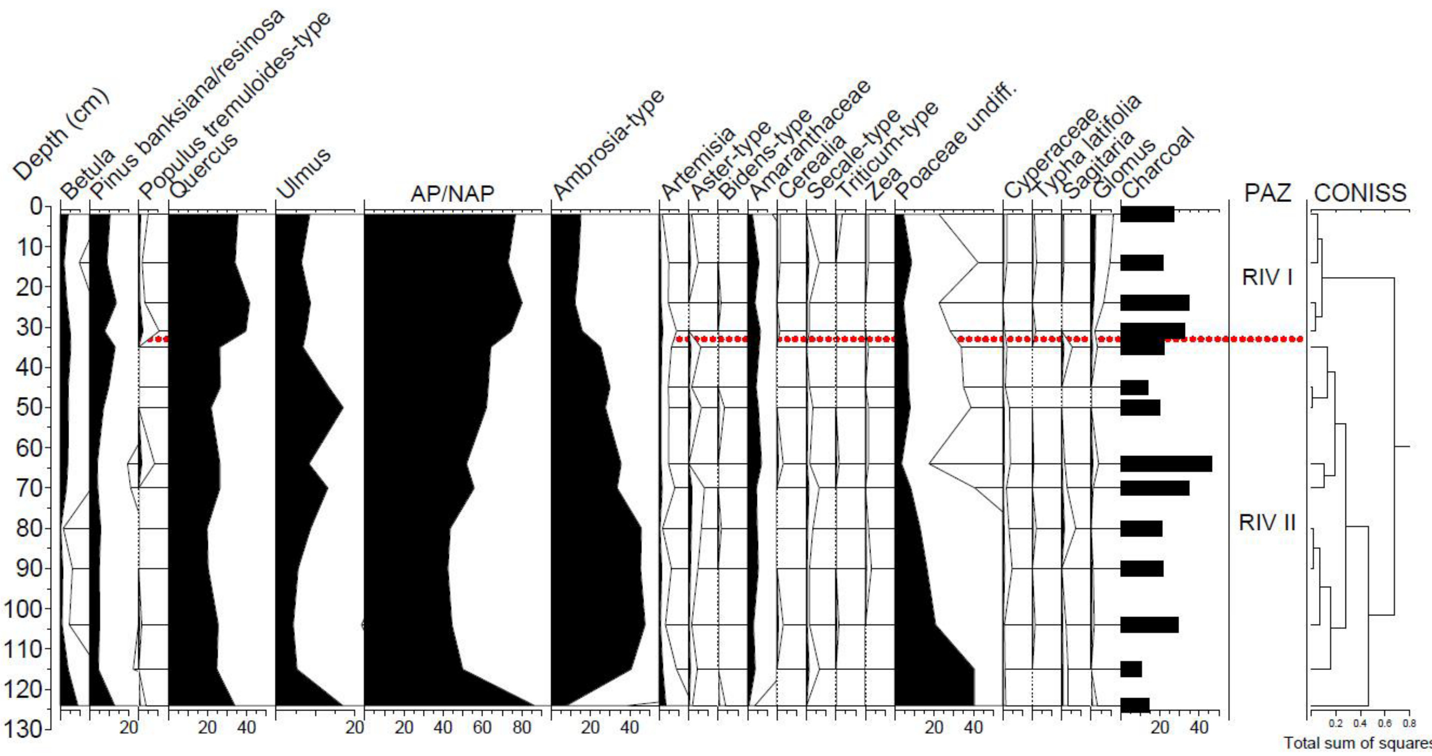


Fig. 11 A. River Lake, Core LOWMIN2-RIVL19-1A. Pollen percentages of the major pollen types

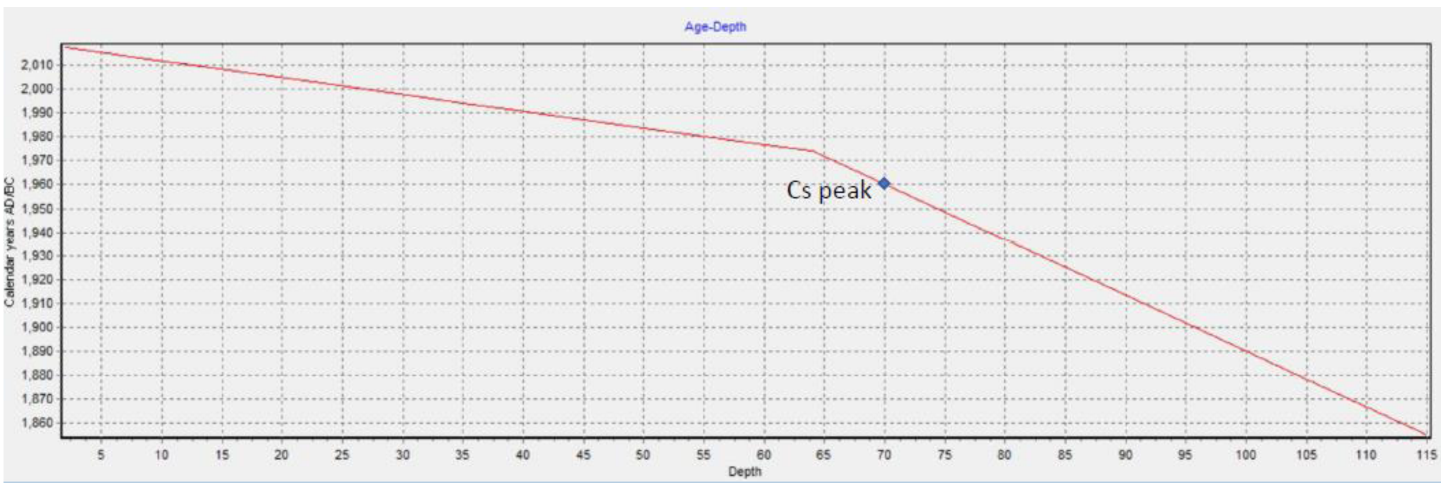


Fig. 11 B. River Lake depth-age model based on pollen with the position of the Cs peak at 70 cm. According to the model the age for this depth is 1960.

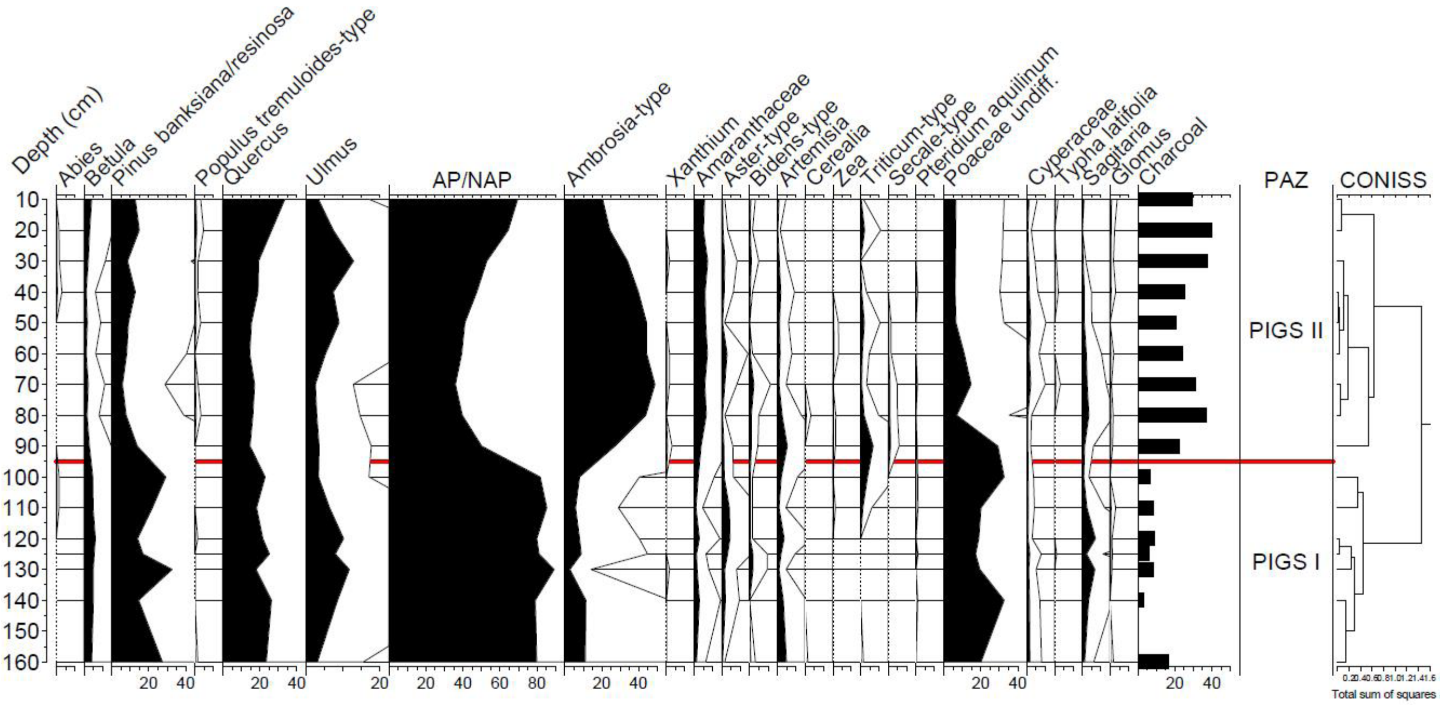


Fig. 12 A. Pig's Eye Lake, core PIGS 19-3A. Pollen percentages of the major pollen types

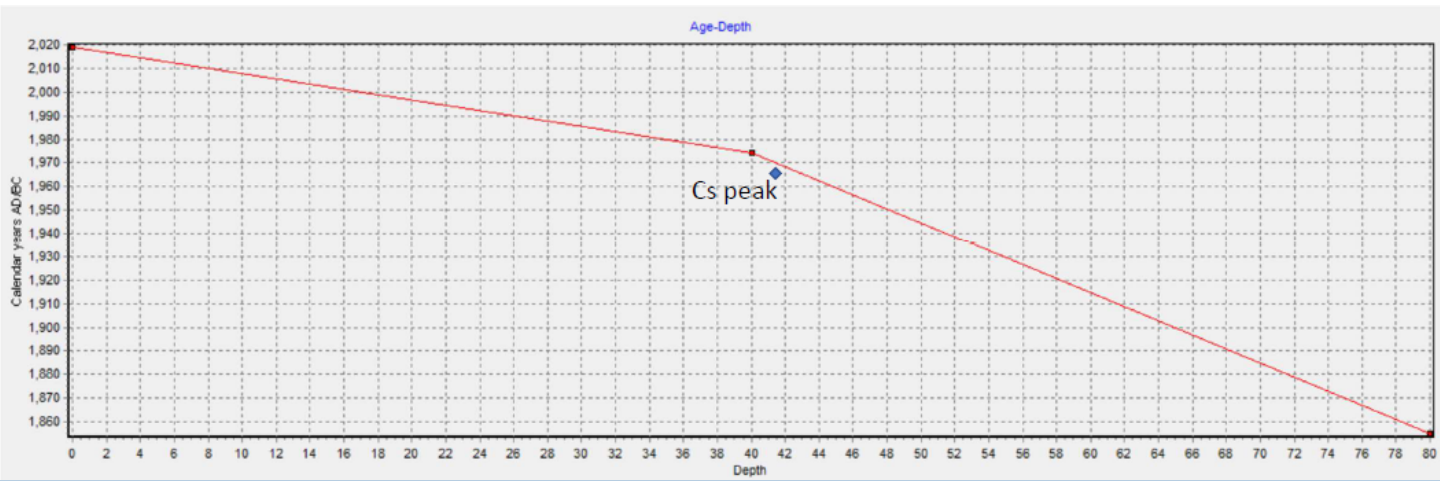


Fig. 12 B. Pig's Eye Lake depth-age model based on pollen with the position of the Cs peak (1963) at 42 cm. The pollen-based age of this point is 1968.

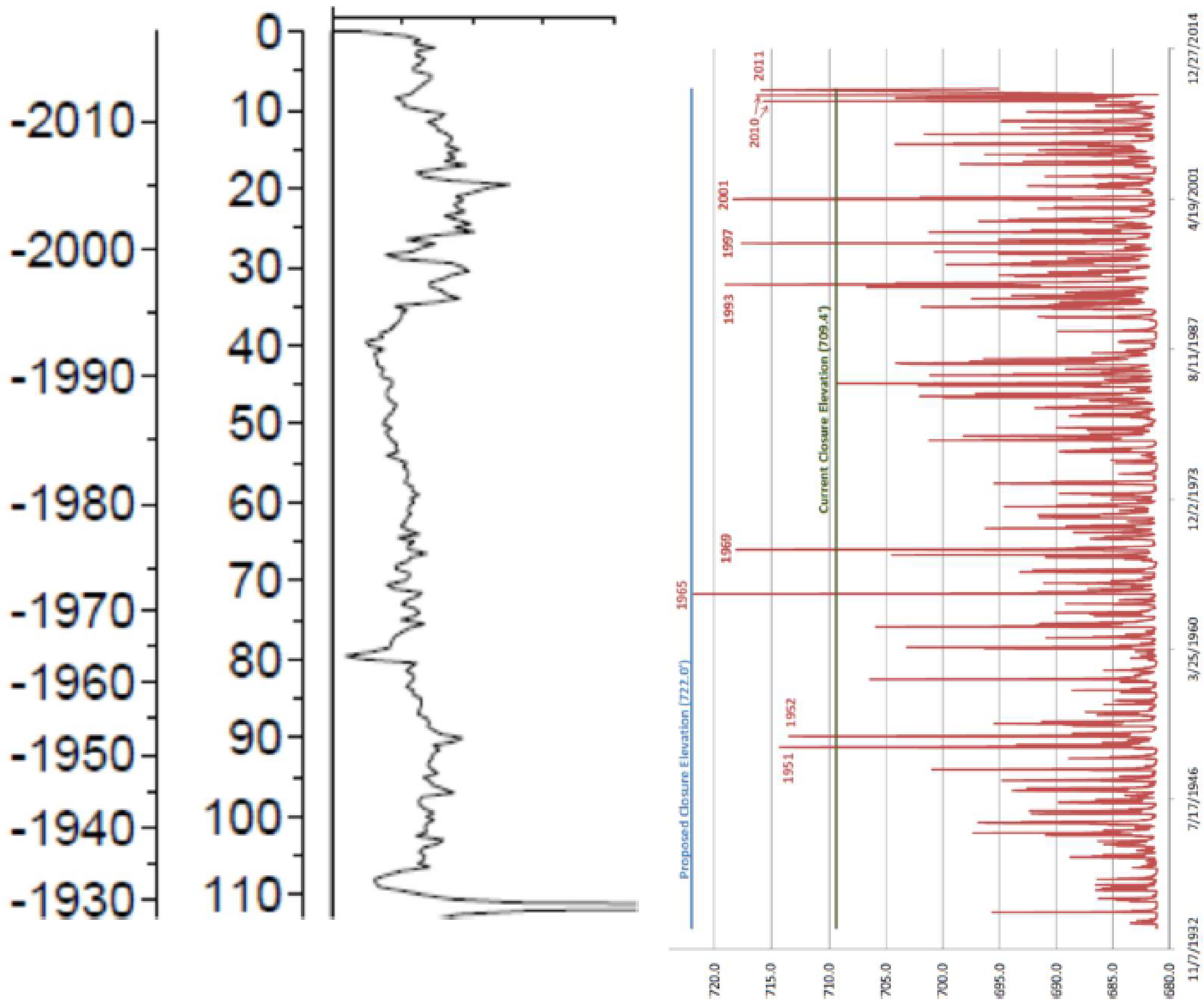


Fig. 13. A plot of the magnetic susceptibility (left) and gauge data on the Minnesota River upstream of Jordan, Minnesota showing historical closures of the bridge at Highway 101 (right). These floods would have impacted Rice Lake. Adapted from Jennings et al., 2019.

ANALYTICAL RESULTS

There were only a limited number of detections of P-N-nonylphenol monoethoxylate and one measurable detection of P-N-nonylphenol in the cores with depth age models. All were just barely above the detection limit of the methodology used by the commercial lab. There was a detection in Rice Lake of 0.17 mg/kg or 170 ppb at over 70cm deep in the core, but that core does not have a depth-age model to say when this occurred. These results

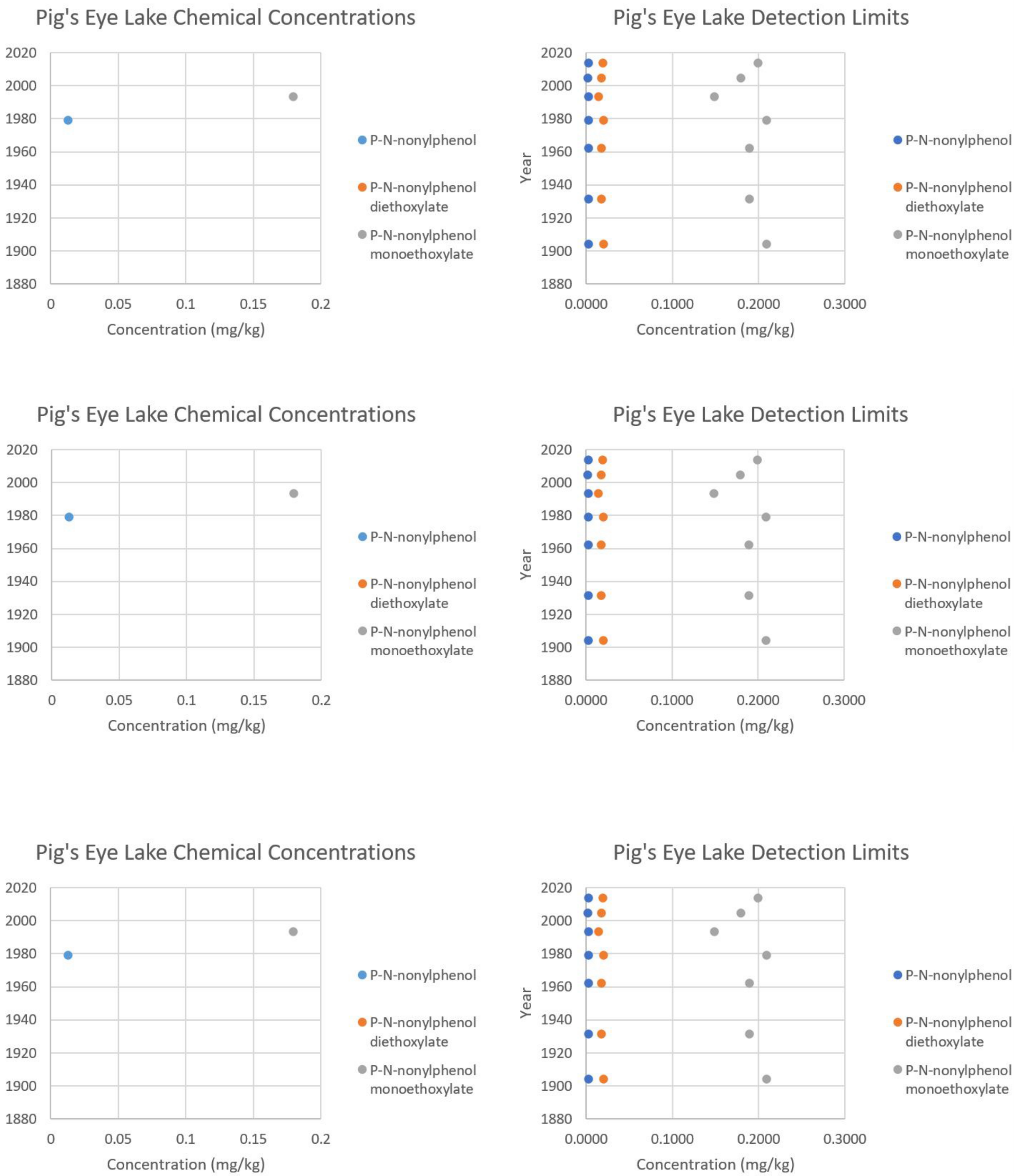


Fig. 14 Plots of the detected compounds and the detection limits for three lakes. 1 mg/kg = 1,000 ppb.

do not suggest either a temporal trend or a spatial pattern (Fig. 14). However, they are enough to document the presence of the compound in sediment in the past. Detections in the earlier work of Crane (2018) were on the order of 20–40 ng/g or ppb.

Discussion

The expectation was that concentrations of the contaminants would be similar to those reported by Crane (2018, 2019). What we saw instead was only one or two detections per core and at one to two orders of magnitude higher level. We would have preferred an even lower detection limit, but that was not achievable. However, because P-N-nonylphenol monoethoxylate and P-N-nonylphenol were detected in the cores in the range of decades for which the compound was widely used, but at just above the detection limit, we suspect that it is present elsewhere and at lower concentrations that were not detectable by this lab. This was a new procedure for Legend Analytical—however, the spikes were recovered, so the methodology they developed appears to have worked. Legend chemists also expressed concern that there may have been interference with other constituents in core (e.g. salts and carbon).

The pandemic lockdown of labs that stored the cores prevented access to them in an optimum timeframe. The cores were stored in a cold room for almost a year prior to being sampled and then for three months at the lab before the final tests were performed. As a result, there remain questions regarding possible mobilization or degradation of the contaminants.

UPDATED SEDIMENTATION RATES IN RIVERINE LAKES

This work allowed for a refined calculation of sedimentation rates in Minnesota River floodplain lakes. Previous estimates for Rice Lake using an undated, pollen-based stratigraphy (Jennings et al., 2019) were:

1 cm/y -1	1860 to 1910
1.0 cm/y -1	1910 to 1950
2.44cm/y -1	1950 to 1993
1.4 cm/y -1	1993 to 2018

Current calculated rates benefit from a chronology anchored by cesium dating and the newly recognized elm-pollen decline. They are comparable and slight differences may be a result of averaging over what may have been the highest rate of sedimentation in the four decades after 1950.

	1855-1974	1974-2019
River Lake	0.4 cm/yr	1.4 cm/yr
Pig's Eye Lake	0.3 cm/yr	0.9 cm/yr
Rice Lake	0.9 cm/yr	1.6 cm/yr

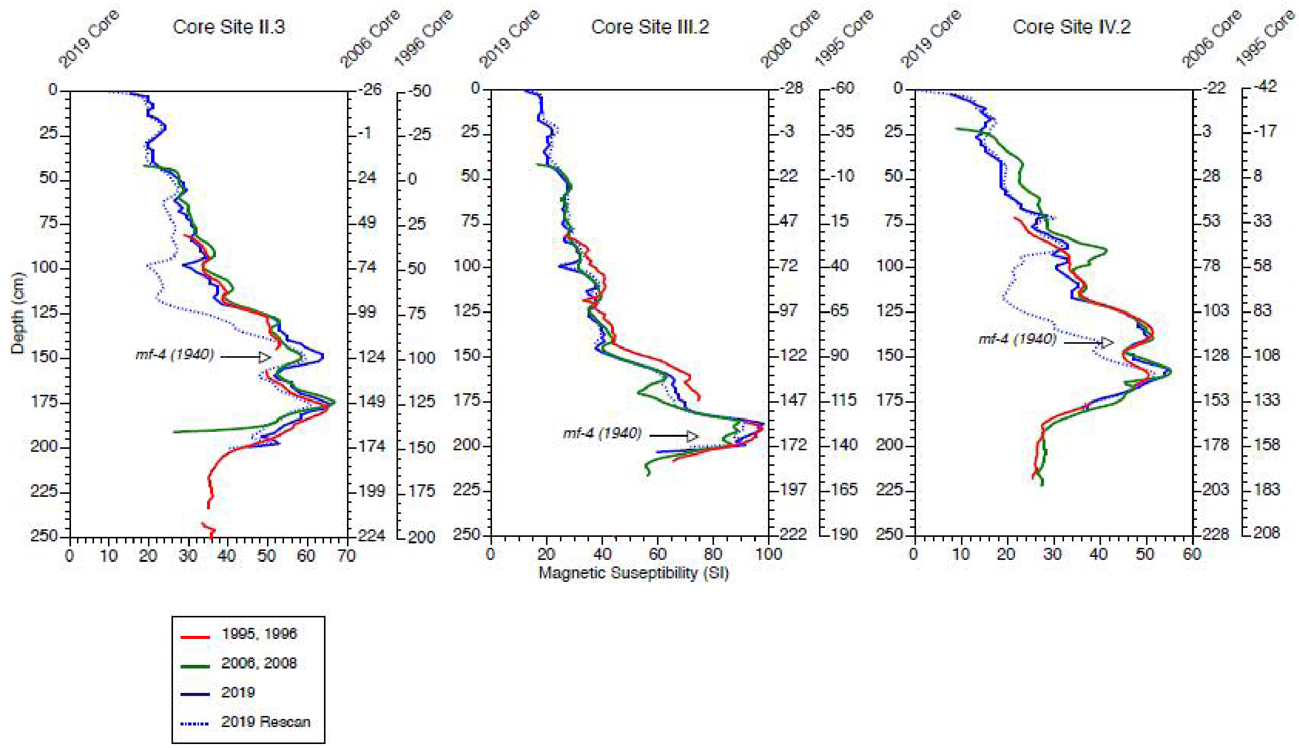


Fig. 15 Use of magnetic signature to correlate cores taken at different times in Lake Pepin

PEPIN RE-CORE CORRELATION AND DATING

The 2019 cores from Lake Pepin (locations given in Table 1) were matched stratigraphically with the dated 1995–1996 master cores (Engstrom et al. 2009) and re-cores from 2006–2008 based on whole-core magnetic susceptibility according to methods outlined in Blumentritt and others (2013). The magnetic profiles were visually correlated by graphing them on the same depth scale and shifting the vertical offset until the peaks and valleys matched most closely. Magnetic readings at the end of core sections and several spurious magnetic peaks associated with pieces of boiler slag (clinkers) in the 2006 cores were deleted from the graphs to make it easier to match profiles. As seen in Fig. 14, the match between the three widely spaced dates is extremely good in most cases.

However, there are some notable discrepancies in the magnetic scans of the 2019 cores repeated in 2021. The scans were repeated to obtain higher stratigraphic resolution (0.5 cm) as compared to the original scans (2.0 cm), but there was a clear loss of magnetic signal in the midsections of two of the rescanned cores (II.3 and IV-2), likely a result of diagenesis of ferromagnetic mineral grains during storage. Fortunately, the original (coarse resolution) 2019 scans could be readily matched to their master cores as well as the 2019 re-scans. Based on visual inspection, the uncertainty in the core matching is estimated at ± 2 cm at all three core sites. The vertical offset from the master cores, which represents the amount of sediment accumulated from 1995/96 to 2019, ranged from 42 cm at site IV.2 to 60 cm at site III.2. The offset from the 2006/08 cores ranged from 22 cm (IV.2) to 28 cm (III.2).

The next step was to determine the location of the sediment surface at 1995–1996 in the 2019 cores. This was done according to cumulative dry mass (g/cm2) rather than core depth (cm) in order to remove the confounding effects of sediment compaction and water loss with the accumulation of new sediment. Correlation points were selected near the top of the 1995–1996 magnetic profiles (32 cm) and added to the vertical offsets (50, 60, and 42 cm for sites II.3, III.2, and IV.2, respectively) to give the correlation depths in the 2019 cores (82, 92, and 74 cm; sites II.3 to IV.2, in that order). The cumulative dry mass at these correlation points in the 2019 cores was then calculated based on dry density data (g dry mass/cm3 wet sediment). Finally, the mass of new sediment deposited between 1995–1996 and 2019 was calculated by subtracting the mass between the correlation points and the top of the 1995–1996 cores (based on dry mass data from the 1995–1996 cores). A similar calculation was done for the difference between the 2006–2008 and 2019 cores

The accumulated mass (1995–1996 – 2019) divided by the time elapsed gives the mean dry mass accumulation rates for the last two and a half decades. These rates at core sites II.3 and III.2 are about 1.0 g cm-2 yr-1, which is not substantially different from their respective (core-specific) rates for 1990–1996 as determined from the master cores (Engstrom et al., 2009; Blumentritt et al. 2013). However, the 1995–2019 rate at core site IV.2, (0.60 g cm-2 yr-1) is about 50% lower than it was in the 1990–96 period. The calculated DMAR values for the two intervals between repeat coring (1995–1996 – 2006–2008) and 2006–2008 and 2019) were effectively the same at all three core sites. A distinct magnetic peak (mf-4) evident in all Pepin cores and originally dated to c. 1940 (Engstrom et al., 2009) occurs in the 2019 cores at 145–149 cm at core site II.3, 193-197 cm at site III.2, and 142-146 cm at site IV.2. Dates in the 2019 cores were interpolated based on mean DMAR for the period 1995–1996 – 2019 and determined by stratigraphic correlation with the 1995–1996 master cores for the period prior to 1995–1996. Calculations are shown in Appendix 7.

Conclusion and Future Work

The riverine lakes on the floodplains of the lower Minnesota and Mississippi rivers and Lake Pepin archive sediment, pollen, and chemicals linked to land use in the greater Twin Cities metropolitan area. We have established or refined the chronologies established for these lakes. The cores are archived providing an opportunity for sampling for other constituents of interest that do not degrade. Pig's Eye Lake may be of particular interest for a broader contaminant history given the of land use in that area.

The low detection of NE and NPE should not be taken as an indication of their absence. There may have been issues related to long core storage and others involving lab procedures that were impossible to overcome in this project.

The novel finding that the elm decline is a reliable feature in the pollen stratigraphy and a useful time marker means improved stratigraphic resolution for the decades after the cesium peak, especially since that peak is decaying with time.

Sedimentation rates remain high in these floodplain lakes on the Minnesota and Mississippi rivers.

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Rob McManus came to work with Freshwater as an intern in the summer of 2019 as a rising junior from Saint John's University, in Collegeville, Minnesota. He was supported by a Barry Goldwater Scholarship and had a goal of learning about lake-sediment coring to document the history of a contaminant.

Discussions with Minnesota Pollution Control Agency (MPCA) scientists led to a selection of nonylphenol and its ethoxylates, a class of compounds that act as endocrine disrupting chemicals and have broad industrial and municipal uses. Although this began as a one-summer project, he returned to it the following pandemic summer and other experienced researchers contributed their time and skills to the work.

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APPENDIX 1: METADATA FOR CORING SITES

Location	Date	Vessel	Water Depth	State	County	Latitude	Longitude	Elev. (m)	Original ID	Core Length	Sed Depth	Sed Depth Bottom
River Lake	7/8/19	Canoe	1.88	MN	Dakota	44.8082	-93.0178	208	LOWMIN2-RIV19-1A-1P-1	132.5	0	1.37
River Lake	7/8/19	Canoe	1.88	MN	Dakota	44.8082	-93.0178	208	LOWMIN2-RIV19-1A-2B-1	99	1.37	2.36
River Lake	7/8/19	Canoe	1.88	MN	Dakota	44.8082	-93.0178	208	LOWMIN2-RIV19-1B-1P-1	96.5	0	0.745
River Lake	7/8/19	Canoe	1.72	MN	Dakota	44.811008	-93.014997	208	LOWMIN2-RIV19-2A-1P-1	133	0	135
Snelling Lake	7/11/19	Canoe	2.59	MN	Hennepin	44.88015	-93.186903	214	LOWMIN2-SNE19-1A-1P-1	140.5	0	1.4
Rice Lake	7/11/19	Canoe	3.19	MN	Carver	44.813936	-93.515542	212	LOWMIN2-RIC19-1A-1A-1	132	0	1.32
Rice Lake	7/11/19	Canoe	3.19	MN	Carver	44.813936	-93.515542	212	LOWMIN2-RIC19-1B-1B-1	98.5	1.22	2.24
Rice Lake	7/11/19	Canoe	3.19	MN	Carver	44.813936	-93.515542	212	LOWMIN2-RIC19-1B-2B-1	53.5	2.24	2.775
Pig's Eye Lake	7/23/19	Canoe	1.79	MN	Ramsey	44.919450	-93.027523	208	LOWMIN2-PIGS19-1A-1P-1	99.5	0	0.95
Pig's Eye Lake	7/23/19	Canoe	1.74	MN	Ramsey	44.915557	-93.023049	208	LOWMIN2-PIGS19-2A-1P-1	92	0	0.87
Pig's Eye Lake	7/23/19	Canoe	1.89	MN	Ramsey	44.915903	-93.028417	208	LOWMIN2-PIGS19-3A-1P-1	135	0	1.31
Pig's Eye Lake	7/23/19	Canoe	1.89	MN	Ramsey	44.915903	-93.028417	208	LOWMIN2-PIGS19-3B-1B-1	67	101	1.68
Pig's Eye Lake	7/23/19	Canoe	1.89	MN	Ramsey	44.915903	-93.028417	208	LOWMIN2-PIGS19-3C-1P-1	145	0	1.41
Pig's Eye Lake	7/23/19	Canoe	1.89	MN	Ramsey	44.915903	-93.028417	208	LOWMIN2-PIGS19-3D-1P-1	90	0	0.90
Pig's Eye Lake	7/23/19	Canoe	1.74	MN	Ramsey	44.915588	-93.032245	208	LOWMIN2-PIGS19-4A-1P-1	93.5	0	0.91
Pig's Eye Lake	7/23/19	Canoe	1.73	MN	Ramsey	44.912342	-93.030269	208	LOWMIN2-PIGS19-5A-1P-1	106	0	1.02

APPENDIX 2: INITIAL CORE DESCRIPTION AND IMAGERY

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APPENDIX 3: LOSS ON IGNITION DATA (ZIPPED)

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APPENDIX 4: ANALYTICAL CHEMISTRY REPORT

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APPENDIX 5: CALCULATIONS FOR PEPIN SEDIMENTATION RATES

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