Analysis of Sediment Cores to Assess Chlorinated Bornanes and Chlorinated Bornenes in the St. Louis River

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United States Environmental Protection Agency
Great Lakes National Program Office
77 West Jackson Boulevard
Chicago, IL 60604

By the

Minnesota Pollution Control Agency
520 Lafayette Rd.
St. Paul, MN 55155

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TABLE OF CONTENTS

In order to minimize paper consumption, the appendices were not printed with every report. If you would like a copy of the appendices (74 pages), please contact Patti King at the MPCA (651) 296-8723 or patricia.king@pca.state.mn.us

Introduction

This project used chlorinated bornane/bornene profiles in dated sediment cores collected downstream of former industrial discharges to the St. Louis River and from a control site to determine whether there was a significant local source of these chemicals to the St. Louis River.

Background

Chlorinated bornanes and bornenes are the primary constituents of toxaphene. Toxaphene is a complex mixture of persistent, bioaccumulative, chlorinated chemicals that were manufactured in the U.S. from 1947 to 1982 for use as an insecticide. Toxaphene was predominantly used in the southeastern U.S. on agricultural crops. However, it was also used in Minnesota as an agricultural insecticide and as a piscicide in fish management programs.

The manufacture of toxaphene was banned in the United States in 1982 due to its persistence, toxicity and potential to bioaccumulate. It is classified as a probable human carcinogen by the USEPA and potentially affects the liver, kidneys, adrenal glands, immune system and fetal development (ATSDR, 1996).

Toxaphene has been detected globally, including the air, water, sediments and fish of the Great Lakes (Hoff et al., 1993; De Vault et al., 1996; Pearson et al., 1997; Glassmeyer et. al., 1997). Because of its persistence, toxicity and bioaccumulative potential, toxaphene has been designated as a zero discharge chemical in the Binational Agreement to Restore and Protect Lake Superior. It is also listed as a Level One Substance in the Great Lakes Binational Toxics Strategy and therefore targeted as an immediate priority for virtual elimination in the Great Lakes Basin.

In Minnesota, the MPCA has qualitatively detected toxaphene in sediments at ten locations in the Duluth/Superior Harbor. Subsequent quantitative analysis of six of these samples measured toxaphene concentrations ranging from 60 to 204 ng/g (MPCA, unpublished data). As a comparison, Lake Superior surficial sediment concentrations have been measured at 3 to 15 ng/g (Pearson et al., 1997). The MPCA has also intermittently measured toxaphene in water discharging to Lake Superior from the Duluth-Superior Harbor at concentrations exceeding the Minnesota water quality standard for toxaphene (MPCA, 1999). The presence of toxaphene in Lake Superior has resulted in the Province of Ontario issuing fish consumption advisories in Lake Superior due to elevated levels in sportfish.

The dominant source of toxaphene (chlorinated bornanes/bornenes) to Lake Superior is thought to be atmospheric deposition (Swackhamer and Hites, 1988; Pearson et. al., 1997; Swackhamer et al., 1999). However, the dominance of non-point source loading to Lake Superior as a whole does not preclude local impacts due to point sources. Because of the presence of chlorinated bornanes/bornenes in the Duluth-Superior Harbor and Lake

Superior, the MPCA is interested in determining whether there has been or is currently a local source of these chemicals to the St. Louis River Area of Concern.

Toxaphene was synthesized by the chlorination of camphene, resulting primarily in chlorinated bornane/bornene constituents. Since wood from pine trees contain relatively high levels of camphene-like terpenes, the bleaching of wood pulp from pine trees has been suggested as an unintentional source of toxaphene-like chemicals (chlorinated bornanes/bornenes) to the environment (Larson and Marley, 1988; Stuthridge et al., 1990). Studies testing this hypothesis have not been definitive due to methodological difficulties in replicating the pulp bleaching process. Historically, pine wood was an important source of wood pulp for pulp mills discharging waste to the St. Louis River. Because of this, the St. Louis River provided an excellent opportunity to determine the historical inputs of chlorinated bornanes and bornenes to this watershed and to assess the relative contributions from atmospheric deposition and point source discharges.

Due to uncertainty regarding the origins of the chlorinated bornanes/bornenes in this study, we will most often refer to the chemicals quantitated in this project as chlorinated bornanes and bornenes rather than toxaphene. The term toxaphene will still be used when appropriate (e.g. referring to the pesticide or technical standards used to quantitate environmental chlorinated bornanes/bornenes and referring to other studies that use the term toxaphene).

Site Description

The St. Louis River Watershed has an area of 3010 square miles and is the second largest tributary to Lake Superior with a mean annual discharge of 66 cubic meters per second (MPCA and WDNR, 1992). In the early 1900s, several hydroelectric dams were constructed on the lower St. Louis River, resulting in reservoirs that have trapped several feet of sediment behind the dams. Historically, there were numerous industrial and municipal dischargers to the St. Louis River including several pulp mills in the Cloquet area which is approximately 23 miles upstream of the mouth of the river. The first pulp mill on the St. Louis River was owned by Northwest Paper Company. It began operating around 1900 and produced ground wood pulp. In 1914, a sulphite pulp mill was added (Northern Lumber Company documents in the Minnesota Historical Society Archives). By the early 1930s, additional pulp mill discharges to the St. Louis River included bleached soda, bleached Kraft and bleached sulphite (Lockwood Directory, 1934). In 1979, all effluent discharges except non-contact cooling water were re-routed to the Western Lake Superior Sanitary District wastewater treatment plant which discharges into the Duluth/Superior Harbor. If any of these bleached pulp discharges contributed chlorinated bornanes to the St. Louis River, evidence of elevated inputs during active discharge to the river should be preserved in the chlorinated bornane/bornene profile of sediment cores collected approximately 16 miles downstream.

Project Objectives

This project compares chlorinated bornane/bornene profiles in dated sediment cores collected from the control site and the downstream test site to assess whether bleached

pulp mill discharges may have been a historical source of these chemicals to the St. Louis River. The cores collected from the control lake represent inputs from atmospheric deposition alone. The chlorinated bornane/bornene profile in the St. Louis River cores represents inputs from atmospheric deposition and from historical discharges to the river upstream of the site (including, but not limited to the pulp mill discharges mentioned above).

The following objectives were set in order to test this hypothesis:

1. Determine total chlorinated bornane/bornene concentrations and accumulation rates over time in dated sediment cores from the St. Louis River below historical discharges and at a control site.
2. Determine the time of onset of chlorinated bornane/bornene accumulation in sediments of the St. Louis River below historical discharges to the St. Louis River and in sediments of a control site subject only to atmospheric deposition.
3. Compare ratios of peak to present day accumulation rates between the control and test sites.
4. Compare total chlorinated bornane/bornene:chlordane ratios between control and test sites.
5. Compare the relative rates of decline in total chlorinated bornane/bornene accumulation in the 1980s between the control and test sites.
6. Compare the relative homolog distribution at specific time intervals within and between sites.

The data from the above objectives will allow us to assess the relative inputs of chlorinated bornanes/bornenes to the St. Louis River from ambient atmospheric deposition and past industrial and municipal discharges. There are several pieces of information that will be used to assess the significance of historical effluent discharges as sources of chlorinated bornanes/bornenes to the St. Louis River.

- If the former paper mill discharge was a significant contributor of chlorinated bornanes/bornenes to this system, the onset of accumulation should occur earlier in the downstream core relative to the control core. The paper mill began discharging bleached pulp effluent to the river by the early 1930s, while the insecticide toxaphene was not commercially produced until 1947.
- If a point source discharge in the Cloquet area was a significant source of chlorinated bornanes/bornenes to the St. Louis River, the accumulation rates (and possibly concentrations) in the downstream cores should be significantly greater than those in the control cores. To compare between sites, the ratio of peak to present day accumulation rates in the control core will be compared to the corresponding ratio in the test core. Using the ratio of historical to present day measures will account for the effect the unequal-sized watershed of these two sites when comparing concentrations or accumulation rates between cores.

- A similar strategy will be employed using chlorinated bornane/bornene:chlordane ratios. The environmental fate and transport of chlordane is similar to that of chlorinated bornanes/bornenes. However, it is not known to be associated with any of the historical discharges to the St. Louis River. Therefore, the ratio of total chlorinated bornane/bornene to chlordane ratio should be significantly greater in the test core if there was a significant point source of chlorinated bornanes/bornenes to the St. Louis River.
- If there was a significant point source of chlorinated bornanes/bornenes to the St. Louis River, the decline in accumulation at the test site should be sharper than the decline in accumulation at the control site. The decline in chlorinated bornane/bornene input at the control site will be due predominantly to the U.S. ban on toxaphene production in 1982, while the decline in inputs to the test site will be due to the ban on toxaphene manufacture and the re-routing of all point-source discharges to WLSSD in 1979.
- In the absence of point source inputs, the relative homolog distribution of chlorinated bornanes/bornenes in sediment cores above and below the former discharge should be similar, assuming that at any given point in time both sites received similar inputs from atmospheric deposition. A notably different homolog and or congener distribution between the two sites may indicate a source other than (or in addition to) atmospheric inputs.

Methods

Site Selection

Three test sediment cores were collected from a backwater area below the Fond du Lac Dam (Figure 1). This site is a depositional area approximately 7 miles upstream from the mouth of the river and 16 miles downstream of the historical pulp mill discharges. It is above the known contaminated industrial sites in the St. Louis River Estuary and above the influence of river flow reversals due to seiche activity in Lake Superior. This site was selected because previous sediment cores were collected from this area and were successfully dated. The system of dams on the St. Louis River between Cloquet and Fond du Lac results in a fluctuating hydraulic regime resulting in highly variable sedimentation rates and ^{210}Pb fluxes. This variability would have made it very difficult to date sediment cores collected in upstream reservoirs of the St. Louis River using the ^{210}Pb method. Therefore, a backwater area below the lowest dam was selected for the test site.

Considerable effort was spent in identifying an appropriate site to use as a control in this study. Ideally, the control cores would have been collected from a depositional area in the St. Louis River upstream of the historical discharges in Cloquet. However, preliminary work on the St. Louis River indicated that we would be unlikely to find an undisturbed, depositional area upstream of Cloquet. Prior to the commencement of this project, the MPCA collected and dated two sediment cores collected from depositional areas around the Dunlap Islands in the St. Louis River just upstream of Cloquet. The ^{210}Pb profile of these cores indicated that this potential control site was less than

acceptable due to sediment mixing and potential scouring (Dr. Daniel Engstrom, personal communication). The MPCA and Dr. Engstrom then assessed the possibility of locating another control site further upstream on the St. Louis River. The use of USGS quadrangle maps indicated that there were not likely to be undisturbed depositional areas in the upper part of the river. Because of this, West Twin Lake in the St. Louis River watershed was selected as the control site for this project (Figure 1). This lake is located approximately 8 miles NW of Cloquet. The lake is 121 acres and has a maximum depth of 18 feet. It has a small amount of development on the east side of the lake and a county park on the west side of the lake with a public boat access. DNR records indicate that toxaphene has not been used in this lake for the purpose of fish management.

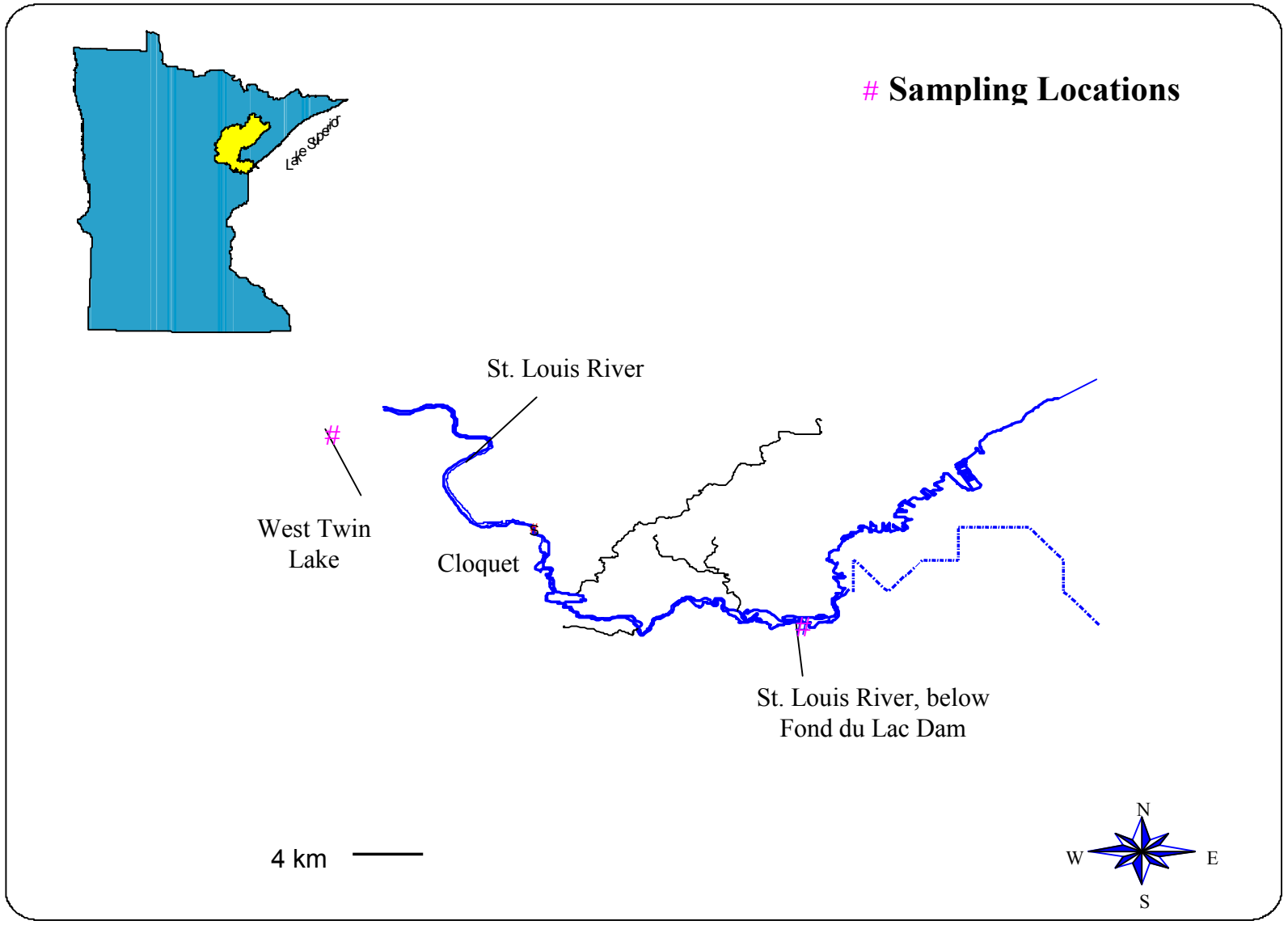
Sediment Core Collection

A total of six sediment cores were collected and sectioned for analysis. Three control sediment cores were collected from West Twin Lake, and three test sediment cores were collected from the St. Louis River.

Sediment cores were collected using a piston corer and rigid drive rods operated from a double-anchored boat. The piston corer had a 7 cm diameter polycarbonate core barrel that collected a continuous core of sediment (Wright, 1991). This piston corer collects the watery, unconsolidated surface sediments as well as deeper strata without disturbance or displacement (core shortening) (Blomqvist, 1985 and 1991).

All cores were at least 1.5 meters in length. The top 1.44 meters were sectioned and preserved as samples. This depth was meant to include pre-1900 sediments. A visual inspection of the core through the polycarbonate core tube and during extrusion was made and notes taken regarding characteristics of the sediment. The cores were held in a vertical position and extruded in 2 cm increments from the sediment-water interface (00 cm) to 48 cm depth in the core. From 48 cm depth to 144cm depth, 4 cm sections were extruded. Samples were collected and stored in pre-cleaned, glass jars with Teflon-lined lids. For most sections, the outside surface of each core section was trimmed off with a stainless steel spatula to remove the outside smear. The top several sections of the core were unconsolidated due to their high water content, and these sections were not trimmed. The unconsolidated sediments were collected in a Plexiglas collar around the core tube and poured/scraped into the sample jars. A note was made regarding the depth at which trimming began for all cores. The depth at which the sediments were consolidated enough to allow trimming the outside layers was approximately 6 – 8 cm in the river cores and 20 – 30 cm in the lake cores. All samples were refrigerated at the St. Croix Watershed Research Station until further processing.

Figure 1. Location of sampling sites. West Twin Lake is the control site. The St. Louis River below Fond du Lac Dam is the test site.



Sample Processing

The sediment sections were homogenized and sub-sampled for the following analyses: ^{210}Pb dating, Loss-on-ignition, ^{137}Cs dating and pollen analysis. Sediments to be dated were freeze-dried prior to analysis. Samples for loss-on-ignition analyses were refrigerated in tightly capped plastic containers until analysis. Samples for the analyses of total organic carbon and contaminants were kept in the original glass sample jars and transported to the University of Minnesota, where they were refrigerated until analysis. Not all analytes were measured in all sections. Results from the initial ^{210}Pb dating were used to direct further specific analyses on specific sections of the core. Eleven sections from each core were analyzed for chlorinated bornanes/bornenes. Sections were selected to represent the following time frames: the time prior to European settlement (early 1800's), the years between when the pulp mills began discharging and before toxaphene was produced (1920-1940), the years during which toxaphene was produced (1950-1981), the time after toxaphene was banned (after 1982) and present day.

Analytical Methods

Detailed analytical methods are provided in the Quality Assurance Project Plan for this project (Appendix A). A brief description of the methods is provided here.

^{210}Pb Dating

Sediment cores were analyzed for ^{210}Pb activity to determine age and sediment accumulation rates for the past 150 years. Lead-210 was measured in 18 - 22 sections in each core through its grand-daughter product ^{210}Po using the method of Eakins and Morrison (1978). Dates and sedimentation rates were determined according to the constant rate of supply (c.r.s.) model (Appleby and Oldfield, 1978) with confidence intervals calculated by first-order error analysis of counting uncertainty (Binford, 1990).

Chlorinated Bornane/bornene, Chlordane and Nonachlor

The primary constituents of the pesticide toxaphene are bornanes and bornenes having 6 to 10 chlorines (i.e. hexa - deca chlorinated bornanes/bornenes). These are the homologs quantitated in this project. Chlorinated bornane/bornene concentrations were quantified using electron capture negative ionization (ECNI) mass spectrometry method as described by Swackhamer et al. (1987) and modified by Pearson (1996) and Glassmeyer et al. (1999). Chlordane and nonachlor concentrations were quantified using electron capture negative ionization (ECNI) mass spectrometry concurrently with chlorinated bornane/bornene quantitation.

Ancillary Data

Percent Moisture

Percent moisture was determined gravimetrically by drying a subsample of homogenized sediment to a constant weight in a 60°C oven.

Loss on Ignition

Dry-density (dry mass per volume of fresh sediment), water content, organic content and carbonate content of sediments was determined by standard loss-on ignition techniques

which involve drying a subsample of homogenized sediment overnight at 100 °C and igniting at 550°C and 1000°C for one hour each (Dean, 1974).

Pollen Analysis

Pollen samples from selected increments from each core were prepared according to the Laboratory procedures described by Faegri and Iversen (1975). The pollen analysis provides additional data to confirm the ^{210}Pb dating particularly for older sediments where the error in ^{210}Pb dating is greatest.

^{137}Cs

Selected intervals from the three St. Louis River cores were analyzed for ^{137}Cs to identify sediments deposited during the 1963-1964 peak in atmospheric nuclear testing. This serves as an additional confirmation of the ^{210}Pb dating results.

Quality Control

Detailed QA/QC procedures are provided in the Quality Assurance Project Plan for this project (Appendix A). A brief summary of the procedures is provided here. QA/QC data are provided in Appendix G.

Precision

Overall precision was assessed through analysis of duplicate field samples at a rate of 10%. Analytical precision was assessed through analysis laboratory split samples at a rate of 5%. The relative percent difference between the two samples will be calculated to estimate precision.

Accuracy

The accuracy of ^{210}Pb dating was assessed by comparison to other independent dating markers, specifically the 1963 ^{137}Cs peak and the settlement horizon from the pollen record. The analytical accuracy of the ^{210}Pb procedure was assessed by spiking each sample with a ^{209}Po yield tracer. Chlorinated bornane/bornene, chlordane and nonachlor accuracy was assessed using laboratory matrix spikes and surrogate recovery spikes. Percent recovery for the surrogate and matrix spikes was calculated to estimate accuracy.

Blanks

Field blanks are used to assess contamination from the matrix, sample containers and field equipment involved in sampling. Pre-1900 sediments from deep in each core should contain no measurable chlorinated bornane/bornene or chlordane and were used as sediment field blanks in this study. A laboratory procedural blank was run with each set of samples prepared for extraction and was used to assess contamination resulting from laboratory procedures. Background contamination is not a problem in ^{210}Pb dating, and blanks were not run in this analytical procedure.

Detectability

Analytical sensitivity is defined as the method detection limit (MDL) which is the minimum concentration above which you have confidence that the analyte was present or

not. Dr. Swackhamer's laboratory used field matrix blanks (deep sediment) to determine the MDLs in this project. All sample data were examined as to whether the response is below the MDL. Homologs that are below the MDL are considered as zero when summing to determine total chlorinated bornane/bornenes. Data values less than the MDL were not reported.

Detectable counts in ^{210}Pb dating are ten times the background counts of the detector. Background counts of 10-14 days are made every 5-6 months on each detector. The lowest count ever measured in an environmental sample by this laboratory was over two orders of magnitude greater than the background count of the instrument.

Results

The three St. Louis River sediment cores were analyzed for loss-on-ignition and dated with ^{210}Pb, ^{137}Cs and pollen (Appendices C, D, E and F respectively). The three cores from West Twin Lake were analyzed for loss-on-ignition and dated with ^{210}Pb. Cores for which the data indicated the least post-depositional disturbance and those for which the best dating confirmation could be made with the ^{137}Cs and pollen analysis were selected for contaminant analysis. Cores #1 and #2 from the St. Louis River and cores #4 and #6 from West Twin Lake were selected for additional analysis. Only the analytical results from these four cores will be discussed in this section. However, data from all cores are provided in the appendices. In addition, while a brief discussion of the dating data is provided below, a more detailed summary report submitted by the laboratory that performed the analyses is provided in Appendix B.

The sediment cores were a uniform color of silty material throughout each core. Core #1 from the St. Louis River included a layer of fine sand in silt at 18-20 cm, wood chips and other detritus at 44-52 cm and reddish clay at 52-56 cm. Core #2 from the St. Louis River contained variable amounts of plant fibers in sections 30 through 46, a large layer of plant detritus at 56-60 cm, a red-brown layer with fine fibers at 68-72 and course peat at 80-84 cm. The two cores from West Twin Lake were uniformly silty throughout without any remarkable characteristics. Loss on ignition data are provided in Appendix C.

The average percent organic carbon content of St. Louis River cores #1 and #2 was 8.34 ± 3.39 and 15.94 ± 10.44 respectively. The median percent organic carbon in these two cores was 8.44 and 11.58 percent respectively. Core #2 contained a greater amount of plant fiber throughout the core and course peat material at about 80 cm that accounted for the higher organic content of this core. The average percent organic carbon content of West Twin Lake cores #4 and #6 was 57.8 ± 3.97 and 54.2 ± 3.73 respectively. The median value for these cores was 58.9% and 55.6% respectively. The higher organic content of the lake cores is due to greater erosional contributions to river sediments relative to lake sediments that receive relatively greater inputs of biologically-derived material.

Sediment cores collected from both the St. Louis River and West Twin Lake were dated successfully. Sediment ^{210}Pb dating and sedimentation rate data are provided in Appendix D. In general, the data indicated that sedimentation rates have always been greater in the St. Louis River (0.0432 - 0.406 g/cm^2/yr) than in West Twin Lake (0.0114 - 0.0354 g/cm^2/yr), and rates in both locations began increasing in the late 1800's or early 1900's. Increased logging, settlement and agriculture probably resulted in increased watershed erosion into these water bodies.

Hexa - deca chlorinated bornane/bornene concentrations were typically below the method detection limit (MDL) in all cores. Only five samples had concentrations above the method detection limit (MDL) of this study (Table 1). The MDL was 36 ng total hexa - deca-chlorinated bornane/bornenes per sample extract. On a mass/mass basis, the method detection limit varied as a function of the sediment mass extracted for analysis, ranging from 4.5 - 36 ng/g sediment. This project-specific MDL was higher than anticipated due to decreased instrument sensitivity. The large number of non-detects in the sample set are due to the low concentrations in the sediments, the increased MDL and the limited sample mass available for extraction.

In the St. Louis River cores, the sections that had detectable concentrations of hexa - deca chlorinated bornanes/bornenes were dated at 1957-1961 and 1978-1981 (core #1) and 1927-1931 and 1974-1978 (core #2). The measured sample concentrations ranged from 6.08 to 10.6 ng/g total hexa-deca chlorinated bornanes/bornenes. There was nothing apparent in the field notes, dating or chemistry data that would explain the occurrence of chlorinated bornanes/bornenes in the 1927-1931 section with only non detect samples above it in the core until 1974. This time frame is prior to the production of Toxaphene pesticide and mixing and diffusion from overlying sediments would require the presence of chlorinated bornanes a/bornenes in the sediments above. It may be that there was mixing and or diffusion from overlying sediments and the overlying sediments had non-detect values due to smaller sample size extracted or the presence of interfering sediment components. Only one sample from West Twin Lake exceeded the MDL with a concentration of 46.1 ng/g. This was in the 1960-1965 section.

Normalized to the organic content of the sample, the St. Louis River concentrations of hexa-deca-chlorinated bornanes/bornenes ranged from 58.2 to 121 ng/g OC. The organic-normalized concentration in the West Twin Lake was 93.3 ng/g OC. The accumulation rate of total hexa-deca-chlorinated bornanes/bornenes ranged from 1.4 - 2.87 ng/cm^2/yr among the four measured values in the St. Louis River cores and was 1 ng/cm^2/yr in the single sample from West Twin Lake. Due to the lack of duplicate data that exceeded the MDL, we are unable to estimate the error associated with the concentrations or contaminant accumulation rates reported.

Table 1. Analytical results for Cores #1 and #2 from the St. Louis River. All sample concentrations in this table have been corrected for surrogate recovery.

Sample ID	Depth of Section (cm)	Date	Sediment Accumulation (g/cm2/yr)	Percent organic	Percent CaCO3	Surrogate recovery* (percent)	Trans-nonachlor (pg/g)	Cis-nonachlor (pg/g)	Trans-chlordane (pg/g)	Cis-chlordane (pg/g)	Total toxaphene (ng/g)	Hexa-chlorinated toxaphene (% of total)	Hepta-chlorinated toxaphene (% of total)	Octa-chlorinated toxaphene (% of total)	Nona-chlorinated toxaphene (% of total)	Deca-chlorinated toxaphene (% of total)
057-293	0-2	1998-1999	0.214	10.8	4.0	74.5	nd	nd	nd	nd	nd					
309-525	2-4	1995-1998	0.256	9.77	3.7	71.4	nd	nd	127	nd	nd					
286-935	12-14	1981-1984	0.322	8.53	3.3	90.8	63.6	46.8	147	116	nd					
162-924	14-16	1978-1981	0.358	8.03	3.3	121.8	58.7	40.4	143	106	6.08	4.6	33.7	61.1		0.6
382-033	16-18	1975-1978	0.358	7.97	3.3	88.2	59.3	44.8	167	145	nd					
866-324	18-20	1972-1975	0.407	7.81	3.1	56.9	77.1	58.1	209	164	nd					
072-177	26-28	1957-1961	0.271	8.71	3.4	106.1	45.1	35.8	196	144	10.6		72.3	2.0	12.1	13.6
645-948	28-30	1953-1957	0.271	9.81	3.8	88.2	61.2	48.5	296	171	nd					
541-809	34-36	1938-1944	0.209	9.15	3.4	79.1	21.0	nd	74.0	nd	nd					
843-222	38-40	1925-1933	0.148	9.09	3.3	37.2	nd	nd	nd	nd	nd					
792-671	52-56	1809-1842	0.0810	5.94	2.7	52.5	nd	nd	nd	nd	nd					

Sample ID	Depth of Section (cm)	Date	Sediment Accumulation (g/cm2/yr)	Percent organic	Percent CaCO3	Surrogate recovery* (percent)	Trans-nonachlor (pg/g)	Cis-nonachlor (pg/g)	Trans-chlordane (pg/g)	Cis-chlordane (pg/g)	Total toxaphene (ng/g)	Hexa-chlorinated toxaphene (% of total)	Hepta-chlorinated toxaphene (% of total)	Octa-chlorinated toxaphene (% of total)	Nona-chlorinated toxaphene (% of total)	Deca-chlorinated toxaphene (% of total)
031-929	0-2	1998-1999	0.209	14.3	4.69	92.1	nd	nd	nd	nd	nd					
512-455	2-4	1996-1998	0.206	12.2	6.41	81.2	nd	nd	nd	nd	nd					
790-680	12-14	1982-1985	0.213	10.5	3.88	68.9	nd	33.0	nd	nd	nd					
992-625	14-16	1978-1982	0.209	10.4	3.64	86.0	32.5	32.6	94.0	135	nd					
161-163	16-18	1974-1978	0.202	10.4	3.83	113	40.6	39.9	102	nd	7.93		23.8	76.2		
916-398	18-20	1970-1974	0.248	10.6	3.72	74.7	68.3	63.5	128	nd	nd					
581-235	24-26	1956-1961	0.195	11.5	4.19	81.7	34.7	38.1	131	nd	nd					
000-852	26-28	1951-1956	0.197	11.5	4.27	85.5	37.9	23.4	189	162	nd					
574-075	32-34	1937-1942	0.173	11.7	4.00	84.1	nd	nd	nd	nd	nd					
517-108	36-38	1927-1931	0.186	12.9	4.25	87.6	nd	nd	nd	nd	7.52	99.0			0.981	
504-692	60-64	1825-1861	0.0432	12.4	3.02	69.2	nd	nd	nd	nd	nd					

Table 1. Analytical results for Cores #4 and #6 from West Twin Lake. All sample concentrations in this table have been corrected for surrogate recovery.

Sample ID	Depth of Section (cm)	Date	Sediment Accumulation (g/cm2/yr)	Percent organic	Percent CaCO3	Surrogate recovery* (percent)	Trans-nonachlor (pg/g)	Cis-nonachlor (pg/g)	Trans-chlordane (pg/g)	Cis-chlordane (pg/g)	Total toxaphene (ng/g)	Hexa-chlorinated toxaphene (% of total)	Hepta-chlorinated toxaphene (% of total)	Octa-chlorinated toxaphene (% of total)	Nona-chlorinated toxaphene (% of total)	Deca-chlorinated toxaphene (% of total)
760-174	0-2	1997-1999	0.0276	55.4	5.17	88.4	nd	nd	nd	nd	nd					
195-657	2-4	1994-1997	0.0261	54.4	5.28	70.2	nd	nd	nd	nd	nd					
398-492	8-10	1984-1987	0.0245	52.7	5.98	60.2	nd	nd	nd	nd	nd					
492-942	10-12	1980-1984	0.0230	52.1	5.48	63.6	nd	78.9	nd	nd	nd					
397-239	12-14	1975-1980	0.0213	52.2	4.98	56.6	nd	nd	nd	nd	nd					
028-937	14-16	1970-1975	0.0222	50.9	5.78	56.2	nd	nd	nd	nd	nd					
913-693	18-20	1958-1965	0.0176	50.4	5.42	78.4	57.3	44.2	nd	nd	nd					
784-920	20-22	1951-1958	0.0174	51.1	2.98	65.4	nd	nd	nd	nd	nd					
743-542	26-28	1938-1942	0.0281	58.9	2.08	85.0	nd	nd	nd	nd	nd					
436-853	32-34	1926-1931	0.0228	56.8	4.43	53.9	nd	nd	nd	nd	nd					
417-392	52-56	1835-1852	0.0125	61.9	2.92	66.0	nd	nd	nd	nd	nd					

Sample ID	Depth of Section (cm)	Date	Sediment Accumulation (g/cm2/yr)	Percent organic	Percent CaCO3	Surrogate recovery* (percent)	Trans-nonachlor (pg/g)	Cis-nonachlor (pg/g)	Trans-chlordane (pg/g)	Cis-chlordane (pg/g)	Total toxaphene (ng/g)	Hexa-chlorinated toxaphene (% of total)	Hepta-chlorinated toxaphene (% of total)	Octa-chlorinated toxaphene (% of total)	Nona-chlorinated toxaphene (% of total)	Deca-chlorinated toxaphene (% of total)
854-615	0-2	1997-1999	0.0312	50.48	5.77	57.1	nd	nd	nd	nd	nd					
412-651	2-4	1995-1997	0.0316	50.34	5.53	60.1	nd	nd	nd	nd	nd					
810-049	12-14	1982-1985	0.0323	50.19	5.74	67.3	0	0	240	0	0					
957-804	14-16	1980-1982	0.0354	50.15	5.59	70.2	nd	nd	nd	nd	nd					
643-187	16-18	1977-1980	0.0352	49.98	5.35	58.3	nd	nd	nd	nd	nd					
825-825	18-20	1974-1977	0.0334	49.89	5.06	63.8	nd	nd	nd	nd	nd					
181-693	24-26	1960-1965	0.0217	49.40	5.05	66.0	nd	nd	nd	nd	46.1	70.8	11.2	3.99	8.56	5.40
295-995	26-28	1953-1960	0.0193	49.45	4.67	71.4	nd	50.9	195	nd	nd					
733-209	30-32	1939-1946	0.0171	50.15	4.75	53.9	nd	54.9	nd	nd	nd					
376-679	34-36	1928-1932	0.0292	55.44	4.63	65.3	nd	nd	nd	nd	nd					
439-525	56-60	1832-1851	0.0114	58.35	3.52	63.6	nd	nd	nd	nd	nd					

There are not enough quantitative chlorinated bornane/bornene data to meet all the objectives of this project. The data within all cores were too incomplete to establish a chronological profile and determine dates of onset and peak accumulation. The surficial sediments at all sites were less than the MDL, preventing us from normalizing concentrations at any specific time to watershed size as described in objective #3. In addition, the nonachlor and chlordane data were less than the MDL in the one West Twin Lake section that had detectable chlorinated bornenes/bornanes, again preventing us from normalizing chlorinated bornane/bornene concentrations at any specific time to watershed size as described in objective #4. Therefore we were unable to compare the dates of onset, ratios of peak to present day accumulations, ratios of chlorinated bornane/bornene to chlordane, relative rates of decline or contaminant inventories between the two sites as described in the project objectives.

Assuming that the hexa - deca chlorinated bornanes/bornenes concentrations exceeding the MDL in the St. Louis River cores are the maximum concentrations in the cores (6.08 - 10.6 ng/g), they are less than the concentration of the single sample that exceeded the MDL in the control lake (46.1 ng/g) and are comparable to maximum concentrations measured in sediment cores from Lake Superior and two remote, unimpacted lakes in the Lake Superior Basin (2.8 - 29 ng/g in Lake Superior, 18 ng/g in Siskiwit Lake and 4.9 ng/g in Outer Island Lake) (Pearson et al., 1997). Unfortunately, the comparison of concentrations among these sites is not entirely valid. We have no estimate of the error associated with the contaminant concentrations. Because we are measuring concentrations near the MDL, the associated error may be substantial. In addition, the sedimentation rate varies dramatically among the sites. The St. Louis River has a greater sediment accumulation rate than any of these other sites, and this could dilute the apparent chlorinated bornane/bornene concentrations.

The maximum chlorinated bornane/bornene accumulation rates estimated for the St. Louis River and West Twin Lake were 2.9 and 1.0 ng/cm^2/yr respectively. As with the concentration, a direct comparison of these rates is not possible due to the lack of data. While we have estimates of error associated with the sedimentation rates, without the error associated with the chlorinated bornane/bornene concentrations, we can't calculate the propagated error associated with these accumulation rates. In addition, without a complete contaminant profile we can't be certain that these are the peak concentrations / accumulation rates in the core. Finally, without present-day chlorinated bornane/bornene accumulation rates or matched chlordane data for the West Twin sample, we cannot normalize the accumulation rates to the variable watershed inputs between these two sites.

While the data generated in this project are inadequate to meet the specific stated objectives, the overall results of this study indicate that there has not been a significant point-source of hexa - deca chlorinated bornanes/bornenes to the St. Louis River. There is no evidence of elevated chlorinated bornane/bornene concentrations in the St. Louis River. Even if there has been concentration dilution due to greater erosional inputs to the St. Louis River, it is likely that a large source of hexa - deca chlorinated bornanes/bornenes directly to the river (as would result from approximately 50 years of waste discharge from several pulp-mills) would result in a measurably elevated concentrations at some depth in the downstream cores. We don't see this in either of the river cores. In addition, while chlordane and nonachlor (thought to be primarily atmospherically derived) were detected more often in the St. Louis River cores, the concentrations were similar between the two sites. If the primary source of chlorinated

bornane/bornenes was atmospheric deposition, you would expect to see a similar pattern for these chemicals. If there was a significant point source of hexa - deca chlorinated bornane/bornenes to the St. Louis River, you would expect to see less apparent dilution in the river sediment (relative to atmospheric chlordane/nonachlor), resulting in much higher relative concentrations in the river (i.e. if there was a significant point source of chlorinated bornanes/bornenes to the river, the apparent dilution of this contaminant should be much less than that for chlordane/nonachlor). This is in contrast to the relatively low measured hexa - deca chlorinated bornane/bornene concentrations in the St. Louis River.

Conclusion

The data generated in this project are inadequate to meet the specific objectives of this study due to higher than anticipated detection limits. Nonetheless, while circumstantial, the overall results of the study indicate that there has not been a significant point-source of hexa - deca chlorinated bornane/bornenes or toxaphene to the St. Louis River and that the pulp mill effluent that was historically discharged to the river was not a significant source of these chemicals to the St. Louis River. This conclusion is based on the preponderance of non-detect values throughout the sediment cores and the low concentration of hexa - deca chlorinated bornane/bornenes in samples that did exceed the method detection limit.

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APPENDIX A

Quality Assurance Project Plan

Analysis of Sediment Cores to Assess Chlorinated Bornanes and Chlorinated Bornenes in the St. Louis River

Quality Assurance Project Plan

Grant GL985919-01-0

Submitted to
U.S. EPA Great Lakes National Program Office
and
U.S. EPA Region V
Chicago, IL

By

Minnesota Pollution Control Agency
520 Lafayette Rd.
St. Paul, MN 55155

A1. Approvals

Patricia King, Project Manager, MPCA Date

Kimberly Sandrock, QA Manager, MPCA Date

Daniel Engstrom, Science Museum of Minnesota Date

Deborah Swackhamer, University of Minnesota Date

Edward Klappenbach, Project Manager, U.S. EPA Date

Louis Blume, Quality Assurance Manager, U.S. EPA Date

A2. Table of Contents

List of Tables

A3. Distribution List

Louis Blume
U.S.EPA - Great Lakes National Program Office
77 W Jackson Blvd.
Chicago, IL 60604-3590

Edward Klappenbach
U.S.EPA - Great Lakes National Program Office
77 W Jackson Blvd.
Chicago, IL 60604-3590

Frank Anscombe
U.S.EPA - Great Lakes National Program Office
77 W Jackson Blvd.
Chicago, IL 60604-3590

Kimberly Sandrock
Minnesota Pollution Control Agency
Environmental Outcomes / Monitoring and Assessment
520 Lafayette Rd
St. Paul, MN 55155

Patricia King
Minnesota Pollution Control Agency
Environmental Outcomes / Monitoring and Assessment
520 Lafayette Rd
St. Paul, MN 55155

Daniel Engstrom
Science Museum of Minnesota
St. Croix Watershed Research Station
16910 152nd St. N.
Marine on St. Croix, MN 55047

Deborah Swackhamer
University of Minnesota, School of Public Health
Environmental and Occupation Health
Box 807 Mayo
420 Delaware St. S.E.
Minneapolis, MN 55455

Roger Pearson
University of Minnesota, School of Public Health
Environmental and Occupation Health
Box 807 Mayo
420 Delaware St. S.E.
Minneapolis, MN 55455

A4. Project / Task Organization

Patricia King is the Project Manager, and as such has the responsibility to oversee all aspects of this project. She reports directly to her immediate supervisor, Dan Helwig and to the EPA Project Officer, Edward Klappenbach. She is responsible for coordinating the collection and analysis of samples and the interpretation and reporting of data for this project. Other principal participants in this project include Dr. Daniel Engstrom (Science Museum of Minnesota, St. Croix Watershed Research Station), Dr. Deborah Swackhamer (University of Minnesota) and Dr. Roger Pearson (University of Minnesota).

All sediment core collection and dating will be done by the St. Croix Watershed Research Station. Dr. Engstrom will work cooperatively with the MPCA to identify appropriate sampling locations. He has primary responsibility for collecting sediment cores appropriate for the goals of this project, dating the sediment cores and measuring the necessary lithographic parameters according to the procedures outlined in this QA Plan. The MPCA will assist Dr. Engstrom with sediment core collection. Dr. Engstrom will review all data generated in his laboratory, direct any necessary corrective actions, provide quarterly updates to the MPCA project manager and provide a final interpretive report to the MPCA. Dr. Engstrom will assist the MPCA in interpreting the sediment core contaminant profiles.

All chlorinated bornane/bornene, chlordane and nonachlor analyses will be performed at the University of Minnesota under the direction of Dr. Swackhamer following the procedures outlined in this QA Plan. Dr. Swackhamer will have overall responsibility for the contaminant analyses and seeing that all tasks are completed. She will oversee the extraction and analysis of samples, periodically review lab procedures, review all QA/QC data, provide quarterly updates to the MPCA project manager and provide a final report for the MPCA. Dr. Roger Pearson is a senior scientist on the project and will be responsible for the chlorinated bornane/bornene, chlordane and nonachlor analyses. He will assist in QA review, and he will be responsible for the data collection and electronic compilation. Drs. Swackhamer and Pearson will assist the MPCA in interpreting the results of sediment core contaminant profiles. Anne Lutz (B.S. Chemistry) will perform sediment extractions and cleanup and percent moisture determination. Ms. Lutz will also assist with data management. Percent total organic carbon determination will be performed at the Soils Laboratory of the University of Minnesota.

The laboratories involved in this project are responsible for the ensuring the quality of the data they generate prior to submitting data to the MPCA. Ms. King has responsibility for the overall quality assurance for the project and will review all QA and sample data reported by the laboratories involved in this project prior to final data interpretation.

The results of this project will be made available to data users within EPA and the scientific community at large.

A flow chart of the project organization follows:

Project Coordination: MPCA

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Planning of Field Work: MPCA
Science Museum

⇓

Sample Collection: Science Museum
MPCA

⇑⇓

Sample Analyses: University of Minnesota
Science Museum

⇓

Data Interpretation: MPCA,⇔EPA QA Manager University ofEPA Technical Contact
Minnesota,
Science Museum

⇓

Data Reporting MPCA⇔EPA Project Manager

⇓

Data Users

A5. Problem Definition / Background

This project will use chlorinated bornane/bornene profiles in dated sediment cores collected downstream of former discharges to the St. Louis River and from an unimpacted control site to determine whether there was a significant local source of these chemicals to the St. Louis River.

Chlorinated bornanes and bornenes are the primary constituents of toxaphene. Toxaphene is a complex mixture of persistent, bioaccumulative, chlorinated chemicals that were manufactured in the U.S. from 1947 to 1982 for use as an insecticide. Toxaphene was synthesized by the chlorination of camphene, resulting in primary constituents of chlorinated bornanes. The manufacture of toxaphene was banned in the U.S. in 1982 due to its persistence, toxicity and potential to bioaccumulate. It is classified as a probable human carcinogen by the USEPA and potentially affects the liver, kidneys, adrenal glands, immune system and fetal development (ATSDR, 1996). It has been detected globally, including the air, water, sediments and fish of the Great Lakes (Hoff, 1993; Swackhamer, unpublished data; De Vault, 1996; Pearson, 1997; Glassmeyer et. al., 1997). Because of its persistence, toxicity and bioaccumulative potential, toxaphene has been designated as a zero discharge chemical in the Binational Agreement to Restore and Protect Lake Superior. It is also listed as a Level One Substance in the Great Lakes Binational Toxics Strategy and therefore targeted as an immediate priority for virtual elimination in the Great Lakes Basin. While the historical use of toxaphene is likely to be the dominant source of chlorinated bornanes/bornenes to the ambient environment, we cannot be certain of the origins of chlorinated bornanes/bornenes measured in this study. They may be persistent components of the insecticide toxaphene or incidental byproducts of industrial processes involving chlorine. Because of this uncertainty, we will most often refer to the chemicals quantitated in this project as chlorinated bornanes and bornenes rather than toxaphene. The term toxaphene will still be used when appropriate (e.g. referring to standards used to quantitate environmental chlorinated bornanes/bornenes and referring to other studies that use the term toxaphene).

The presence of toxaphene in Lake Superior has resulted in the Province of Ontario issuing fish consumption advisories in Lake Superior due to elevated levels in sportfish. In Minnesota, the Department of Natural Resources has measured toxaphene concentrations in lake trout collected along the western shore of Lake Superior exceeding the Ontario guideline of 0.2 μg/g (MDNR, unpublished data). The Minnesota Pollution Control Agency has qualitatively detected toxaphene in sediments at ten locations in the Duluth/Superior Harbor. Additional quantitative analysis of six of these samples measured toxaphene concentrations ranging from 60 to 204 ng/g. As a comparison, Lake Superior surficial sediment concentrations have been measured at 3 to 15 ng/g (Pearson et. al., 1997). In addition, a current EPA-funded Duluth-Superior Harbor, Lake Superior Toxics Loading Study has intermittently detected toxaphene in water discharging to Lake Superior from the Duluth-Superior Harbor at concentrations exceeding the Minnesota water quality standard for toxaphene (MPCA, 1999).

The dominant source of toxaphene (chlorinated bornanes/bornenes) to Lake Superior is thought to be atmospheric deposition (Swackhamer and Hites, 1988; Pearson et. al., 1997). However, the dominance of non-point source loading to Lake Superior as a whole does not preclude local impacts due to point sources. Because of the presence of chlorinated bornanes/bornenes in the

Duluth-Superior Harbor and Lake Superior, the MPCA is interested in determining whether there has been or is currently a local source of these chemicals to the St. Louis River Area of Concern.

Since toxaphene insecticide was manufactured by the chlorination of camphene, the bleaching of wood pulp containing camphene-like terpenes has been suggested as an unintentional source of toxaphene-like chemicals (chlorinated bornanes/bornenes) to the environment (Larson and Marley, 1988; Stuthridge et. al., 1990).

The St. Louis River provides an opportunity to study historical inputs of chlorinated bornanes and bornenes to this watershed and assess the relative contributions from atmospheric deposition and point source discharges. Historically, there were several industrial and municipal dischargers to the St. Louis River including the Potlatch Northwest Paper Division kraft pulp mill, the Conwed Corporation acoustic tile manufacturing plant (currently USG Corp.), the Wrenshall Oil Refinery and the Scanlon and Cloquet municipal waste water treatment plants. In 1979, all effluent discharges were rerouted to the Western Lake Superior Sanitary District treatment facility that discharges into the Duluth/Superior Harbor. The MPCA has found that a proportion of the sediment-associated contaminants discharged into the St. Louis River from past industrial and municipal sources in the Cloquet have settled out in downstream reservoirs, and that sediment cores collected in the reservoirs can provide a picture of past contaminant inputs into this environment (Schubauer-Berigan and Crane, 1996). If paper mill effluent or any of the other former discharges were a significant source of chlorinated bornanes/bornenes to the St. Louis River, evidence of elevated inputs during active discharge to the river should be preserved in the chlorinated bornane/bornene profile of sediment cores collected downstream.

A6. Project Description and Schedule

The hypothesis to be tested in this study is that there was an historical point source of chlorinated bornanes/bornenes to the St. Louis River.

The following objectives will be met in order to test this hypothesis:

Determine total chlorinated bornane/bornene concentrations and accumulation rates over time in dated sediment cores from the St. Louis River below historical discharges and at a control site.
Determine the time of onset of chlorinated bornane/bornene accumulation in sediments of the St. Louis River below historical effluent discharges to the St. Louis River and in sediments of a control site subject only to atmospheric deposition.
Compare ratios of peak to present day accumulation rates between the control and test sites.
Compare total chlorinated bornane/bornene:chlordane ratios between control and test sites.
Compare the relative rates of decline in total chlorinated bornane/bornene accumulation in the 1980s between the control and test sites.
Compare the relative homolog distribution at specific time intervals within and between sites.

The data from the above objectives will allow us to assess the relative inputs of chlorinated bornanes/bornenes to the St. Louis River from ambient atmospheric deposition and past industrial and municipal discharges. The overall study strategy is described below.

Two to three sediment cores each will be collected from a background control site in the St. Louis River watershed and from a downstream test site. The control site cores will be collected from a nearby-unimpacted lake in the St. Louis River watershed. These cores will be representative of ambient inputs due solely to atmospheric loadings to the watershed. The test sediment cores will be collected from a depositional area below the most downstream dam on the St. Louis River, near the mouth of the river. The sediment cores from the test site will represent inputs due to ambient atmospheric loadings as well as inputs due to upstream point source discharges.

Lead-210 will be used to date the cores. Lead-210 analysis can provide age information for sediments dating back approximately 150 years and will allow for the direct comparison of accumulation rates and concentrations at specific time intervals and comparison of accumulation onset date in cores collected from the control and test sites. Cs-137 and pollen analyses will be used to confirm the sediment chronology determined by ^{210}Pb.

Sediment cores that are successfully dated will be analyzed for chlorinated bornanes and bornenes, chlordanes and total organic carbon. Sensitive and specific analytical methods will be used to insure accurate analyses of all parameters. This will include the use of gas chromatographic/mass spectrometry operating in the electron capture negative ionization mode for analyses of chlorinated bornanes/bornenes.

Chlorinated bornanes/bornenes will be quantified and the data analyzed at several levels. Total chlorinated bornane/bornene will be measured to compare accumulations and concentrations of these chemicals over time within and between sites. Chlorinated bornanes/bornenes will be quantified at the homolog level to identify changes in the relative homolog distribution over time and between sites. Differences in relative homolog distribution may be due to changes in source composition or preferential environmental partitioning and/or transformation of specific congeners / homolog classes. In addition, congener-specific analyses may be conducted on a subset of chlorinated bornanes in selected samples to increase confidence in the spatial, temporal and compositional trends identified through the analyses of total chlorinated bornanes/bornenes and chlorinated bornane/bornene homologs. Congeners identified as Parlar #26 (also called T2), Parlar #50 (also called T12) and #62 were selected for quantitation because they are recalcitrant components of technical toxaphene and relatively significant components of environmental toxaphene (Stern et al., 1992; Whittle et al., 1997).

In addition, cis- and trans-chlordane and cis- and trans-nonachlor will be quantified. These chemicals are similar to toxaphene with respect to their environmental chemistry, but are not associated with known point source effluents discharging to the St. Louis River. If there was a point source of chlorinated bornanes/bornenes to the St. Louis River, the ratio of chlorinated bornane/bornene:chlordane should be significantly greater in the downstream cores relative to the control cores.

Total organic carbon will also be analyzed in the sediment cores. Because chlorinated bornanes/bornenes are hydrophobic, they preferentially partition into organic compartments of the environment. Thus, total organic carbon may be used to normalize contaminant concentrations to adjust for the variability introduced by differences in sediment composition.

There are several pieces of information that will be used to assess the significance of historical effluent discharges as sources of chlorinated bornane/bornenes to the St. Louis River.
If the former paper mill discharge was a significant contributor of chlorinated bornanes/bornenes to this system, the onset of accumulation may occur earlier in the downstream core relative to the control core, depending on the year in which pulp chlorination was introduced. The paper mill began discharging effluent to the river in 1928, while the insecticide toxaphene was not commercially produced until 1947. The significance of the time of onset in assessing contributions from other discharges in the area would depend on the history of industrial operations in the area and the estimated error in the sediment dating.
If a point source discharge in the Cloquet area was a significant source of chlorinated bornanes/bornenes to the St. Louis River, the accumulation rates (and possibly concentrations) in the downstream cores should be significantly greater than those in the control cores. To compare between sites, the ratio of peak to present day accumulation rates in the control core will be compared to the corresponding ratio in the downstream core. Using the ratio of historical to present day measures will account for the effect of variable sized watershed inputs into the two sites when comparing concentrations or accumulation rates between cores.
A similar strategy will be employed using chlorinated bornane/bornene:chlordane ratios. The environmental fate and transport of chlordane is similar to that of chlorinated bornanes/bornenes. However it is not known to be associated with any of the historical discharges to the St. Louis River. Therefore, the chlorinated bornane/bornene:chlordane ratio should be significantly different between the control and test sites if there was a significant point source of chlorinated bornanes/bornenes to the St. Louis River.
If there was a significant point source of chlorinated bornanes/bornenes to the St. Louis River, the decline in accumulation at the test site should be sharper than the decline in accumulation at the control site. The decline in chlorinated bornane/bornene input at the control site will be due predominantly to the U.S. ban on toxaphene production in 1982, while the decline in inputs to the test site will be due to the ban on toxaphene manufacture and the re-routing of all point-source discharges to WLSSD in 1979.
In the absence of point source inputs, the relative homolog and congener distribution of chlorinated bornanes/bornenes in sediment cores above and below the former discharge should be similar, assuming that at any given point in time both sites received similar inputs from atmospheric deposition. A notably different homolog and or congener distribution between the two sites may indicate a source other than (or in addition to) atmospheric inputs.

This project requires technical expertise in the dating and interpretation of sediment cores and the analysis and interpretation of chlorinated bornanes/bornenes that are not available at the MPCA. This expertise will be acquired through contracting with the Science Museum of Minnesota and the University of Minnesota. Dr. Daniel Engstrom (Science Museum of Minnesota) will provide assistance in identifying appropriate sediment core sampling sites required to meet the goal of this study. Dr. Engstrom (with MPCA assistance) will collect the sediment cores from the control and test sites and perform ^{210}Pb dating and loss-on-ignition measurements of sediment cores. Dr. Engstrom will also arrange for the analysis of pollen and ^{137}Cs as necessary. Dr. Engstrom has extensive experience with sediment core collection, dating and interpretation of contaminant histories. Dr. Deborah Swackhamer and Dr. Roger Pearson will conduct the analyses of chlorinated bornanes/bornenes, chlordane, nonachlor and percent moisture. Dr. Swackhamer will also arrange for the analysis of total organic carbon at the University of Minnesota Soils Laboratory. Dr. Swackhamer and Dr. Pearson have extensive experience in chlorinated bornane/bornene analytical method development and the quantitative analysis and interpretation of ambient chlorinated bornane/bornene data.

The proposed timeline for this project is to collect the sediment cores in June 1999 and complete the dating by December 31, 1999. As the sediment cores are successfully dated, the associated sediment samples will be analyzed for chlorinated bornanes/bornenes, chlordane and total organic carbon. All chlorinated bornane/bornene, chlordane and TOC analyses will be completed by March 31, 2000. Preliminary data analysis and interpretation and a draft report will be completed by July 31, 2000. A final report will be submitted to the EPA Project Officer by September 30, 2000.

Semi-annual progress reports will be provided to the EPA-GLNPO Project Officer. These reports will contain a summary of project progress to-date and projected activities for the following six months. Project records will be available to EPA upon request and will include lab notebooks, instrument data files, final data spreadsheets and QA files containing all precision and accuracy and blank data.

A7. Quality Objectives and Criteria for Measurement Data

Because this is a research project, it is difficult to establish quantitative data quality objectives. The confidence associated with our reported measurements of chlorinated bornanes/bornenes concentrations and accumulation rates in sediments will be a function of the uncertainties in sampling, sediment dating and chlorinated bornane/bornene quantitation. Measurement quality objectives (MQOs) are more appropriate for this project. The acceptable level of uncertainty in chlorinated bornane/bornene concentration data is 50%. The acceptable level of uncertainty in sediment dates is 5 years for sediments less than 50 years old, 10 years for dates between 50 and 100 years old and 20 years for dates more than 100 years old. Dating uncertainty is calculated by first-order propagation of counting error (Binford, 1990). The analytical uncertainty will be calculated from replicate laboratory measurements. Overall uncertainty in chlorinated bornane/bornene concentrations due to sampling and analytical variability will be assessed through the analysis of field duplicates. The chlorinated bornane/bornene and chlordane MQOs are summarized in Table 1. Equations and definitions are found in later sections.

Table 1. Measurement quality objectives for chlorinated bornanes/bornenes and chlordane in sediment.

Requirement	Sample Code	Acceptance Criteria	QC Flag
Holding time	NA	Nine months to extraction	EHT
Reporting Units	NA	ng/g dry wt. (Surrogate corrected)	NA
Instrument detection limit	IDL	Once per project; extrapolate from initial calibration curve	IDL*
Method detection limit	MDL	Once per project; 40 CFR App B pt 136	MDL*
Continuing calibration **frequency** **criteria**	CLS	4 standards with each analytical batch; See performance standard criteria	rerun
Routine detectability **frequency** **criteria**	FLD	 All samples > MDL	MDL*
Blanks:			
Field blanks frequency criteria	FRB	Deepest (pre-1900) sediment from each core 1 per sediment core ≤ MDL	FFR
Laboratory blanks frequency criteria	LPB	solvent 1 per analytical batch (six samples) ≤ MDL	FBK
Performance stds frequency % recovery	LPC	 One per run batch 70% < % recovery < 130%	FPC*
Surrogate stds frequency % recovery	LSS	^{13}C chlordane every sample, blank & std; 50% < % recovery < 150%	FSS
Matrix Spikes frequency % recovery	LMS	spiking standard solution, deep sediment 1 per control site; 2 per test site 50% < % recovery < 150%	FMS
Internal stds frequency criteria	LIS	PCB congener 204 every sample, blank and std; Istd area within 4x average Istd area	FIS
Completeness	NA	90% valid data	
Duplicates			
Field Duplicate frequency criteria	FD1	1 per core < 50% RPD	FFD
Lab Duplicates frequency criteria	LD1, LD2	 1 per control site; 2 per test site < 50% RPD	FDL
Confirmation frequency criteria	CON	 all samples all peaks within acceptable retention times and m/z ratios	UNC

* Criteria that are homolog specific. Individual homologs that are out of control limits will be flagged. Entire sample is flagged if more that 3 homologs are flagged.

Additional flags will be applied to samples as follows:
NSQNot sufficient quantity of sample matrix to conduct an analysis.
LACLaboratory accident destroyed sample or rendered it unsuitable for analysis.
NAINot analyzed due to Interference.
RINRe-injection of the sample extract produced the reported value.
REXRe-prepared sample was used to generate the reported value.
FBKFound in procedural blank at greater than acceptable criteria and reported value may be an overestimate.

Table 2. Measurement quality objectives for ^{210}Pb dating.

Requirement	**Sample Code**	**Acceptance Criteria**	**QC Flag**
Holding time	NA	Six months	EHT
Reporting Units	NA	PCi /g sediment (dry weight)	NA
Instrument detection limit	IDL	Once per project; = 10X background count of 10-14 days	IDL
Method detection limit	MDL	Once per project 10X background count	MDL
Continuing calibration frequency **criteria**	N/A	N/A. Calibration done during initial setup. Isotope peak energies and widths monitored daily by experienced personnel.	rerun
Routine detectability frequency criteria	FLD	All samples > D.L.	MDL
Blanks: **Field blanks** frequency criteria **Laboratory blanks** frequency criteria	LDB	N/A Two per project < 10X background	FBK
Performance stds frequency % recovery	N/A	N/A	
Surrogate stds frequency % recovery		^{209}Po every sample 50 < % Recovery < 100%	FSS
Matrix Spikes frequency % recovery	N/A	N/A	
Internal stds frequency criteria	N/A	N/A	
Completeness	NA	90% valid data	
Duplicates **Field Duplicate** frequency criteria **Lab Duplicates** frequency criteria	FD1	Two per core < 20%	FFD
Confirmation frequency criteria		N/A	

N/A = This MQO is not applicable to the ^{210}Pb dating procedure.

A8. Special Training Requirements / Certification

Personnel trained in the collection and ^{210}Pb dating of sediment cores, the analysis of environmental sediment samples and the instrumental analysis of toxaphene are needed for this study.

The staff at the Science Museum of Minnesota - St. Croix Watershed Research Station have extensive experience with core collection, dating and interpretation of contaminant histories in Minnesota and globally. They have participated in two previous studies of sediments in the St. Louis River system - one in the St. Louis River estuary and a second in the reservoirs of the lower St. Louis River. Collectively, the staff of the St. Croix Watershed Research Station have experience in ^{210}Pb dating of more than 500 sediment cores during the last 15 years, resulting in numerous peer-reviewed publications.

The personnel at the University of Minnesota have extensive experience in the trace level analysis of chlorinated bornanes and bornenes (toxaphene) and in the study of the environmental fate and transport of these chemicals. This laboratory has conducted five major studies of toxaphene fate and transport in the Great Lakes in recent years, including the analysis of toxaphene in dated sediment cores from the Great Lakes. This work has resulted in several peer-reviewed publications. They have also performed toxaphene analyses of Lake Superior and Duluth-Superior Harbor fish and Duluth-Superior Harbor sediments for the Minnesota Department of Natural Resources and the Minnesota Pollution Control Agency.

A9. Documentation and Records

Project documentation will include lab notebooks, instrument (raw) data files, final data (spreadsheets), QA files containing all precision and accuracy and blank data and data analysis output files. These files are available for review on site by the MPCA and the EPA Project Officer. The MPCA will provide semi-annual progress reports to the EPA-GLNPO Project Officer.

The final contaminant data reports from the Science Museum of Minnesota to the MPCA will be in Microsoft Excel or compatible spreadsheets as well as hard copies and will include at least the following data:

MPCA sample ID (field samples)
Lab sample code (field and QA samples)
Depth at top of interval (cm)
Depth of base of interval (cm)
Cumulative dry mass (g/cm^2),
Unsupported Activity (pCi/g)
Error of unsupported Activity ((± s.d.)
Cumulative activity below interval (pCi/cm^2)
Age at base of interval (yr)
Error of age (± s.d.)
Date at base of interval (A.D.)

Sediment accumulation rate (g sediment / cm^2 /yr)
Error in sediment accumulation rate (± s.d.)
Supported ^{210}Pb (pCi/g)
Error of supported ^{210}Pb (± s.d.)
Number of samples used to calculate the supported ^{210}Pb
Cumulative unsupported ^{210}Pb (pCi/cm^2)
Unsupported ^{210}Pb flux (pCi/cm^2/yr)
Interpretive graphs of unsupported ^{210}Pb vs. core depth and sediment accumulation vs. ^{210}Pb
The final contaminant data reports from the University of Minnesota to the MPCA will be in Microsoft Excel or compatible spreadsheets as well as hard copies and will include at least the following data:

MPCA sample ID (field samples)
Lab sample code (field and QA samples)
Sample type (sample, lab blank, matrix blank, lab duplicate etc.)
Date received by the University
Date extracted
Date analyzed on GCMS
% dry weight (g dry sediment / g wet sediment * 100)
% organic carbon (g organic carbon / g dry sediment * 100)
Mass of sediment analyzed (g wet weight)
Mass of analyte recovered for each analyte (ng)
Surrogate recovery
Flag codes indicating QA failures

The MPCA will submit the final project report to the EPA Project Officer. The final report will contain all field results (concentrations, sediment chronologies), QA data (duplicate analyses, field and lab blanks, surrogate spikes, and performance standard spikes) and assessment of precision and accuracy based on duplicates and spike recoveries. Total chlorinated bornane/bornenes (6 to 10 chlorines), homologs (hexa - deca), congeners (if available) and accumulation rates will be reported. An interpretive narrative pertinent to the objectives of the study will be included in the final report. Data generated by the instrument data management systems are electronically transferred to spreadsheets or databases for QA review and further reduction. Final reports are generated from these data files, and data are archived on disk. The final report will be submitted electronically and in hard copy.

SECTION B. MEASUREMENTS AND DATA ACQUISITION

B1. Sampling Process Design

B1.1. Site Selection and Description

Six sediment cores will be collected and sectioned for analysis. Three control sediment cores will be collected from an unimpacted lake in the St. Louis River watershed. The control cores will be representative of ambient inputs due solely to atmospheric loadings to the lake and its watershed. The rationale for using a lake as the control site is discussed below. Three test sediment cores will be collected downstream of known historical industrial discharges to the St. Louis River and above industrial sites in the St. Louis River Estuary. The test sediment cores will be collected above the influence of river flow reversals due to seiche activity in Lake Superior. Because it would be difficult to date sediment cores collected in the reservoirs of the St. Louis River using the ^{210}Pb method, our target area for the downstream sediment cores is below the Fond du Lac Dam, in the upper St. Louis River estuary. The sediment cores from the test site will represent inputs due to atmospheric loadings to the river and its watershed and historical inputs from upstream point source discharges.

An unimpacted lake was selected as the control site because preliminary work on the St. Louis River indicated that we would be unlikely to find an undisturbed, depositional area in the St. Louis River above Cloquet. In the fall of 1998, the MPCA collected and dated two sediment cores collected near the Dunlap Islands in the St. Louis River just upstream of Cloquet. The ^{210}Pb profile of these cores indicated that this potential control site was less than acceptable due to sediment mixing and potential scouring (Dr. Daniel Engstrom, Personal Communication). The MPCA and Dr. Engstrom then assessed the possibility of locating another control site further upstream on the St. Louis River. The use of USGS topographical maps indicated that there were not likely to be undisturbed depositional areas in the upper part of the river. Because of this, an unimpacted lake in the St. Louis River watershed will be used as the control site. The control lake is not meant to represent the St. Louis River specifically. It will be used to estimate chlorinated bornane/bornene inputs to this geographical region due to atmospheric deposition to a waterbody and its watershed. With this in mind, there are two complications involved in comparing contaminant accumulations between the river and the control lake. It should be noted that both of these complications would also apply even if the control site were located in the upper reach of the St. Louis River.

The first complication is the different sized watersheds that contribute a proportion of the toxaphene input to each site. The river site would have a much larger watershed contribution. In order to make a valid comparison between these two sites, the ratio of peak to present day accumulation rates in the control lake will be compared to the corresponding ratio in the test site. Because current loadings are solely atmospheric (i.e. there is no current use of toxaphene nor any suspected point sources to the St. Louis River), using the ratio of historical to present day measures will account for the effect of variable sized watershed inputs into the two sites when comparing concentrations or accumulation rates between cores.

The second complication arises when comparing samples of significantly different sediment composition (i.e. sand vs. organic-rich). However, Dr. Engstrom and the MPCA have considerable experience in sediment collection, analysis and interpretation and will make every effort to collect sediments of comparable composition.

B1.2. Sample Collection Times

Initial sediment core collection will take place in June 1999. If ^{210}Pb dating indicates that any of the cores are not suitable for further chemical analysis, additional cores will be collected. Sediments will be deemed unsuitable if the dating indicates that significant disruptions in sediment accumulation have occurred.

B2. Sampling Methods Requirements

B2.1. Collections

Sediment cores will be collected using a piston corer and rigid drive rods operated from a double-anchored boat. The core will be long enough to represent pre-1900 sediments. The piston corer has a 7 cm diameter polycarbonate core barrel and will be used to collect a continuous core of the upper sediments at all coring sites (Wright, 1991). This device recovers the watery, uncompacted sediment surface as well as deeper strata without disturbance or displacement (core shortening) (Blomqvist, 1985 and 1991). The cores will be held in vertical position and extruded (at 2-4 cm increments) into pre-cleaned, glass jars. A visual inspection of the core through the polycarbonate core tube and during extrusion will be made and notes taken regarding characteristics of the sediment. Dr. Engstrom will have primary responsibility for assessing the quality of the core collected (to the extent possible in the field). If the core is determined to be unsuitable for the objectives of this project, it will be discarded and a new core collected. The outside surface of each core section will be trimmed off with a stainless steel spatula to remove the outside smear. The top several sections of the core will be unconsolidated due to their high water content. These sections will not be trimmed. The unconsolidated sediments will be collected in a plexiglass collar around the core tube and poured/scraped into the sample jars. All samples will be refrigerated at the St. Croix Watershed Research Station until further processing.

B2.2. Sample Processing

The sediment sections will be sub-sampled for the following analyses: ^{210}Pb dating, Loss-on-ignition, ^{137}Cs dating, pollen analysis, TOC and contaminant analysis. A subsample of each core section will be transferred to plastic jars and stored at the St. Croix Watershed Research Station for ^{210}Pb dating, Loss on Ignition, pollen analysis and ^{137}Cs dating. Sediments to be dated will be freeze-dried prior to analysis. Samples for loss-on-ignition analyses will be refrigerated in tightly capped plastic containers until analysis. Samples for the analyses of TOC and contaminants will be kept in the original glass sample jars and transported to the University of Minnesota, where they will be logged in, checked for cracks or breakage and immediately refrigerated until analysis. Not all analytes will be measured in all sections. Results from the initial ^{210}Pb dating will be used to direct further specific analyses on specific sections of the core.

B2.3. Sampling Equipment

The St. Croix Watershed Research Station will provide sediment coring equipment and plastic containers for storing sediments for dating and LOI. The MPCA will provide a boat and operator for fieldwork, GPS equipment, notebooks, cleaning materials and clean glass jars for storing sediment for contaminant analyses.

B2.4. Reagents and Containers

The core tube will be cleaned by washing with Alconox detergent and rinsing with site water. All glassware used in the ^{210}Pb procedures will be acid washed. All glassware used in the contaminant lab will be cleaned by covering in foil and ashing for a minimum of four hours at 450°C. Pre-cleaned glass jars with Teflon-lined lids will be used for storing the samples for contaminant analysis.

B2.5. Container Labeling

The samples will be uniquely coded with a sample code in the format of xxx-xxx/nn-nn. Where xxx-xxx is a randomly generated number pre-printed onto sample labels. The nn-nn is the depth at the top of the section - depth at the bottom of the section in centimeters. The use of a randomly generated sample code conceals the identity and location of the core. Labeling the depth of each section allows the contaminant laboratory to estimate the appropriate amounts of toxaphene internal and surrogate standards to add to each sample based on its relative depth in the core and estimated atmospheric inputs. It also allows the laboratory conducting the ^{210}Pb-dating to adjust the mass of sediment counted based on the relative depth in the core and expected amount of native ^{210}Po.

All pertinent station and sample information will be cross-referenced with the sample ID and recorded in a field notebook or laptop computer at the time of collection. The following information will be recorded for each sediment core collected: Date, time, site, station, shoreline characteristics, weather condition, water depth, core depth, duplicates or field blanks collected and the uncorrected GPS coordinates. The following information will be recorded as the core is sectioned: Sample ID, depth at top of section, depth at bottom of section, notable characteristics of sediment section (if any) and whether the outside of the section was trimmed off. All sampling locations will be marked on a USGS Quad map and latitude and longitude will be recorded using a Pathfinder Basic GPS system. All cross-referenced field information will be recombined with the sample ID at the time of data interpretation.

B3. Sample Handling and Custody Requirements

Because no enforcement implications are involved in this project, no strict chain of custody procedure will be used for sample tracking. Samples will be in the custody of the MPCA, the St. Croix Watershed Research Station and the University of Minnesota at all times, including collection, transport, storage and analysis. Once collected and subsampled, samples for contaminant analyses will be refrigerated at the University of Minnesota Environmental Chemistry Laboratory until extraction. Sediment extraction for contaminant analysis will take place within nine months after sample collection. Sample instrumental analyses will take place within three months after sample extraction. Sample extracts will be kept in the laboratory

freezer until analysis. Laboratories containing samples, extracts, analytical standards and logbooks are securely locked with keypad entry. Samples for dating will be freeze-dried and stored at the St. Croix Watershed Research Station. The integrity of all samples and sample containers will be examined upon collection, prior to storage and prior to analysis in the laboratory; those samples having questionable integrity will be noted with the appropriate QC code (e.g. LAC for lab accident) and set aside. All samples collected will be documented in a tracking sheet as part of the overall project files. The custodian of the overall project file is Patti King. The custodian of the laboratory files and sediment subsamples for chlorinated bornane/bornene, and associated ancillary data is Dr. Swackhamer. Dr. Engstrom is the custodian of the laboratory files and sediment subsamples related to ^{210}Pb dating and associated ancillary data.

B4. Analytical Methods Requirements

A summary of analytical methodologies is included below.

B4.1. ^{210}Pb Dating

Sediment cores will be analyzed for ^{210}Pb activity to determine age and sediment accumulation rates for the past 150 years. Lead-210 will be measured in 18 - 22 sections in each core through its grand-daughter product ^{210}Po. All dating of sediments will be completed by December 31, 1999.

B4.1.a. Preparation for ^{210}Pb Dating.

Approximately 1 - 3 g of freeze-dried sediment are spiked with a calibrated ^{209}Po standard to act as a yield tracer. The sample is then digested with concentrated HCl. The Po isotopes are then distilled from a 0.5 N HCl solution and plated onto silver planchets for counting (Eakins and Morrison, 1978).

B4.1.b. Instrumental Analysis

^{210}Po activity will be measured for 1-3 x 10^5 seconds with ion-implanted or Si-depleted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported ^{210}Pb will be estimated from the asymptotic activity at depth (the mean of the lowermost samples in a core). Dates and sedimentation rates will be determined according to the constant rate of supply (c.r.s.) model (Appleby and Oldfield, 1978) with confidence intervals calculated by first-order error analysis of counting uncertainty (Binford, 1990).

B4.2. Chlorinated Bornane/bornene, Chlordane and Nonachlor

Chlorinated bornanes/bornenes will be analyzed at three levels in selected sections of each sediment core; total chlorinated bornane/bornene (6 to 10 chlorines), homologs (hexa - deca) and a subset of congeners (Parlar congeners #26, 50 and 62). Total chlordane will be measured as cis- and trans-chlordane and cis- and trans-nonachlor. All analyses will be completed by March 31, 2000.

B4.2.a. Sample Preparation.

The sediment sample is warmed to room temperature, homogenized and a subsample (≥ 10g) is mixed with anhydrous sodium sulfate (approx. 1:7 wt/wt). The sediment-sodium sulfate mixture is place in a Soxhlet extractor and a known amount of surrogate standard (^{13}C-chlordane) is added to monitor the efficiency of laboratory procedures. The concentration of ^{13}C-chlordane is adjusted to be within an order of magnitude of the expected concentration of chlorinate bornane/bornenes in the samples.

B4.2.b. Sample extraction

The sediment- sodium sulfate mixture is first extracted with 300 mL of methanol for four hours. Then, 300 mL of dichloromethane (DCM) is added to the extractor and cycled for an additional 16-24 hours. The extract is than solvent exchanged to hexane and volume-reduced to approximately 10 mL using a Kuderna-Danish apparatus and steam table.

B4.2.c. Extract Cleanup

Interferences are removed using normal phase column chromatography. Extracts are loaded onto liquid-solid chromatography columns (25 cm x 1.5 cm i.d.) containing from top to bottom: 2 g ashed sodium sulfate (450°C for 8 hours); 4.5 g silica gel (300°C for 8 hours; 0% deactivated); 1 g ashed sodium sulfate; 6 g alumina (1% deactivated wt/wt); 1 g ashed sodium sulfate; 1 g HCl-cleaned copper; ashed glass wool plug. The columns are eluted with 175 mL of 15% (v/v) DCM in hexane followed by 50 mL of 40% (v/v) DCM in hexane. Chromatographic conditions are adjusted to have the chlorinated bornanes/bornenes present in the first fraction. The second fraction is collected in an amber bottle and stored in a freezer. The archived second fraction will be analyzed for carryover if the surrogate recovery falls below the acceptable criteria. In addition, if a procedural or matrix spike sample recovery is below acceptable criteria, the archived second fraction will be analyzed for carryover in all samples prepared in the same batch as that QA sample.

The sample extract is solvent-exchanged to hexane, volume-reduced to approximately 4 mL, transferred to an amber vial and stored at 4°C until analysis.

B4.2.d. Instrumental Analysis

Prior to instrumental analysis the extract is volume-reduced to approximately 100 µL by gently passing purified nitrogen over the sample. An internal standard (PCB congener #204, 2,2',3,4,4',5,6,6'-octachlorobiphenyl) is added to the extract. Chlorinated bornane/bornene concentrations will be quantified using electron capture negative ionization (ECNI) mass spectrometry method as described by Swackhamer et al. (1987) as modified by Pearson (1996) and Glassmeyer et al. (1999). This is done by selective ion monitoring (SIM) of the M^- chlorine cluster for the hexa-chlorinated bornanes/bornenes and the $(M\text{-}Cl)^-$ cluster for the hepta- through deca-chlorinated bornanes/bornenes. Retention time windows have been established by running a toxaphene standard and plotting the abundance of the hexa- through deca- homolog quantitation ions per the methods described by Pearson (1996). Chlordane and nonachlor concentrations will be quantified using electron capture negative ionization (ECNI) mass spectrometry concurrently with chlorinated bornane/bornene quantitation. The ion clusters monitored for chlordane and nonachlor quantitation are provided in Table 3.

A Hewlett Packard 5988A GC/MS is used in the ECNI mode to quantify chlorinated bornane/bornenes, chlordanes and nonachlors. The ionization gas is methane, with the ion source operated at 125°C and about 1 torr pressure. A 60 m x 0.25 mm, 0.25 µm film thickness DB-5 column and helium carrier gas are used in the GC portion of the instrument. The carrier gas flow is approximately 40 cm/sec. The GC operating conditions are 1 µL injection in splitless mode; injector temperature 270°C; initial temperature 80°C, hold 1 minute; 80 - 210-°C at 10°C/minute; 210 - 250°C at 0.8°C/minute; 250-290°C at 10°C/minute; hold 5 minutes. The transfer line is held at 290°C. This program and associated data acquisition method are run by

Hewlett Packard ChemStation software.

Selected ions for the quantitation and confirmation of each bornane/bornene homolog and quantitation of each chlordane class are monitored. These ions are shown in Table 3. The Swackhamer et al. (1987) toxaphene quantitation method determines the total area for a given quantitation ion across a given retention time window (Table 4) and uses this area to calculate the mass of that homolog. An improvement to this method has been made (Glassmeyer et al., 1999) and will be used in this project. The Glassmeyer et al., 1999 method provides for exact confirmation of each peak used in the quantitation, thus providing for a more validated and consistent result. All peaks in a given ion chromatogram (both quantitation and confirmation ions) are individually integrated, with visual confirmation by the operator that the integration parameters result in appropriate baselines. The ratio of the areas of the quantitation and confirmation ions having the same retention time (± 0.1 minute) is calculated and compared to the expected ratio for that homolog. If the ratio is ≥ 20% of the expected (Table 3), the peak is not considered further. Thus, only peaks meeting retention time and confirmation ratio criteria are included in the quantitation. The standards are processed in the same manner as samples. If the criteria are met, the area of each peak is then corrected for ^{13}C and chlordane interferences. These interference-corrected areas are then summed to determine the total area for that homolog. Total chlorinated bornane/bornene area is determined by summing the areas of the hexa- through deca- homologs. The mass of chlordane and nonachlor is determined from the area of the quantitation ion. The equations for calculating analyte mass and concentration are provided in Section B10.

The chlorinated bornane/bornene homolog composition in a sample, expressed as a fraction, will be determined by dividing the area of a given homolog as determined by the Glassmeyer method by the total chlorinated bornane/bornene area (sum of all homolog areas). The fraction may be multiplied by the total chlorinated bornane/bornene concentration to obtain the concentrations of each homolog.

Chlorinated diphenyl ethers (CDPEs) can interfere with chlorinated bornane/bornene quantitation due to their similar mass spectra. Most of them will elute in the second fraction of column cleanup. Our dual filters of retention time match and ion ratios eliminate their further interference. Only those peaks that match retention times to peaks in a toxaphene standard are considered, and then the ion ratios must be within strict limits of expected bornene/bornane homolog ratios to be quantitated. The penta-chloro diphenyl ethers have similar ions as the hexachloro bornanes/bornenes, but the ion ratios are different because of the different number of chlorines. A standard of mixed CDPEs will be run through the quantitation program prior to sample analyses to demonstrate the lack of interference.

Every instrumental batch run includes four calibration standards, up to 12 samples and a minimum of one performance standard. The four calibration standards run at the beginning of each analytical batch consist of the toxaphene standard, the chlordanes and the nonachlors. The four calibration standards range in concentration such that they will bracket the samples being quantitated. This is done because the response factor is not linear at low levels. A performance standard of one of the four calibration standards (concentration chosen varies) is run at the end

of the analytical batch as a check sample. If congeners are quantified in this study, they will be quantified using separate standards in a separate analytical run. The toxaphene standards are obtained from Hercules. The toxaphene congener standards are obtained from ProChem. Chlordane and nonachlor standards are obtained from Ultra Scientific. The ^{13}C-chlordane standard is obtained from Cambridge Isotopes. The PCB congener 204 standard is obtained from Ultra Scientific.

Table 3. Ions monitored in the single ion monitoring (SIM) mode for the quantitation of chlorinated bornanes/bornenes, chlordane and nonachlor.

Empirical formula	**Molecular weight**	**Ion cluster monitored**	**Quantitation ion**	**Confirmation ion**	**Theoretical ion ratio C/Q**
Cl-bornane/ene					
$C_{10}H_{10}Cl_6$	340	M	342	344	0.85
$C_{10}H_{12}Cl_6$	342				2.0
$C_{10}H_9Cl_7$	374	M-Cl	343	341	1.2
$C_{10}H_{11}Cl_7$	376				0.5
$C_{10}H_8Cl_8$	408	M-Cl	377	375	1.1
$C_{10}H_{10}Cl_8$	410				0.45
$C_{10}H_7Cl_9$	442	M-Cl	413	411	1.5
$C_{10}H_9Cl_9$	444				0.95
$C_{10}H_6Cl_{10}$	476	M-Cl	449	447	2.1
$C_{10}H_8Cl_{10}$	478				1.2
Chlordane					
$C_{10}H_6Cl_8$ (cis)	410	M	410	408	1.14
$C_{10}H_6Cl_8$ (trans)	410		406	408	0.34
Nonachlor					
$C_{10}H_5Cl_9$ (cis)	444	M	444	442	1.3
$C_{10}H_5Cl_9$ (trans)	444		444	442	1.3

Table 4. MS-SIM program windows. Three separate ions are collected across each desired mass level to ensure maximum area counts are generated (e.g. 342.81, 342.88, and 343.00 are monitored for the 343 m/z.

Window	Start time	Stop time	6 Cl Tox	7 Cl Tox	8 Cl Tox	9 Cl Tox	10 Cl Tox	trans nona	cis nona	trans chlor	Cis chlor	^{13}C-t-chlor	PCB 204
	e		x	x	x	x							
1	22.0	26.0	x										
2	26.0	28.8	x	x									
3	28.8	29.4								x		x	
4	29.4	29.8	x	x									
5	29.8	30.8						x			x		
6	30.8	33.0	x	x									
7	33.0	35.8	x	x	x								
8	35.8	36.5	x	x	x				x				
9	36.5	41.8	x	x	x								
10	41.8	47.4	x	x	x	x							
11	47.4	48.3			x	x							x
12	48.3	54.7			x	x							
13	54.7	58.7			x	x	x						
14	58.7	78.0					x						

B4.3. Ancillary Data

B4.3.a. Percent Moisture

At the time of contaminant extraction, a subsample (approx. 1 g) is weighed into a tared, ashed aluminum boat and dried to a constant weight (determined by a minimum of two weighings) in a 60°C oven. The percent moisture is the initial wet weight minus the dry weight divided by the initial wet weight times 100. The percent dry weight is 100 minus percent moisture.

B4.3.b. Organic Carbon

Approximately 1 g of dried sediment from the percent moisture determination is placed in an ashed vial and transported to the U of M Soils Laboratory. The samples are combusted at 950°C using a CHN elemental analyzer. Final concentrations are determined from a 4-point calibration curve generated at the same time as the samples. The Soils Lab includes check samples as part of their quality assurance protocols. Data are reported as g OC/g dry sediment. Duplicates will be run at 10% inclusion.

B4.3.c. Loss on Ignition

Dry-density (dry mass per volume of fresh sediment), water content, organic content and carbonate content of sediments will be determined by standard loss-on ignition techniques as described by Dean (1974). Sediment samples of 1 -2 g will be dried overnight at 100 °C and ignited at 550°C and 1000°C for one hour each. Mass measurements will be made of the wet samples and after each heating on an electronic analytical balance. Dry density will be calculated from water content and fixed densities for organic, carbonate and inorganic fractions.

B4.3.d. Pollen Analysis

Pollen samples from selected increments from each core will be prepared according to the Laboratory procedures described by Faegri and Iversen (1975). A known quantity of Eucalyptus pollen will be added to selected samples as a tracer to permit calculation of pollen concentration. Residues will be mounted in silicon oil, and pollen identified under magnifications of 400X and 1000X. At least 300 terrestrial pollen grains will be counted in each sample.

B4.3.e. ^{137}Cs Dating

Selected core intervals will be analyzed for ^{137}Cs to identify sediments deposited during the 1963-1964 peak in atmospheric nuclear testing. Freeze-dried sediments will be measured for ^{137}Cs at 667 keV using a high-resolution germanium diode gamma detector and multichannel analyzer. Detector efficiency will be determined using an NIST-certified source with mineralogical composition similar to the samples.

B5. Quality Control Requirements

The Method Quality Objectives are provided in Section A7. (Table 1). The definitions and equations for assessing attainment of QC objectives are provided below.

B5.1. Precision

Precision is a quantitative measure of the agreement between two or more measurements of the same parameter. It provides a measure of relative uncertainty about a given measurement. Overall precision will be assessed through analysis of duplicate field samples at a rate of 10%. Analytical precision is assessed through replicate analysis of the sample.

For duplicate measurements, the relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|M(s) - M(d)|}{[(M(s) + M(d)]/2} \times 100\%$$

where

RPD = relative percent difference

M(s) = measurement in the sample

M(d) = measurement in the duplicate

For replicate measurements where n>2, precision is described by the relative standard deviation which is calculated as follows:

$$\text{RSD} = \frac{s}{\bar{x}} \times 100\%$$

where

s = the standard deviation of the replicates = $\sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}$

x = the individual analyte measurement
$\bar{x}$ = mean of replicate analyte measurements
n = the number of replicates

To estimate the uncertainty associated with a calculated value that is based on several independent measurements, the propagated uncertainty must be calculated using individual estimates of precision for each measurement.

For addition and subtraction

$$E = \sqrt{(S_1)^2 + (S_2)^2 + \ldots (S_n)^2}$$

where
E = Error associated with the overall value
S_1 = absolute uncertainty (standard deviation) in independent measurement 1
S_2 = absolute uncertainty (standard deviation) in independent measurement 2
S_n = absolute uncertainty (standard deviation) in independent measurement n

For multiplication and division

$$\%E = \sqrt{(\%S_1)^2 + (\%S_2)^2 + \ldots (\%S_n)^2)}$$

where
%E = Percent relative error associated with the overall value
$\%S_1$ = Percent relative uncertainty (RSD) in independent measurement 1
$\%S_2$ = Percent relative uncertainty (RSD) in independent measurement 2
$\%S_n$ = Percent relative uncertainty (RSD) in independent measurement n

B5.2. Accuracy

Accuracy is the degree of agreement between an observed value and an accepted reference value. It provides a measure of absolute uncertainty about a given measurement. The accuracy of ^{210}Pb dating will be assessed by comparison to other independent dating markers, specifically the 1963 ^{137}Cs peak and the settlement horizon from the pollen record. The analytical accuracy of the ^{210}Pb procedure will be assessed by spiking each sample with a ^{209}Po yield tracer. Chlorinated bornane/bornene, chlordane and nonachlor accuracy will be assessed using laboratory spikes and surrogate recovery spikes. The surrogate for chlorinated bornane/bornenes will be ^{13}C-chlordane. Matrix spikes will consist of field matrix blanks (deep, pre-1900 sediment) spiked with representative levels of the toxaphene standard, the cis and trans-chlordanes and the cis and trans-nonachlor and treated as a sample through the analytical procedure.

The percent recovery for the surrogate and matrix spikes is calculated according to the following formula:

%R = [Measured / Actual] X 100%

where
%R = percent analyte recovery
Q(m) = quantity of spike analyte measured in the sample
Q(sp) = quantity of spike analyte added to the sample

B5.3. Representativeness

Representativeness expresses the degree to which a sample from a given site is representative of that site or area, and the matrix from which it was taken and to what degree the sample accounts for analyte heterogeneity in the matrix.

Representativeness is dependent upon the proper design of the sampling program. Sampling representativeness in this project will be maximized by locating our test site near the mouth of the river to integrate total contaminant loadings from the upstream portion of the river and the associated watershed. The selection of an unimpacted control site will ensure that it is representative of ambient atmospheric inputs to the watershed. Analytical representativeness will be maximized by thoroughly homogenizing the sample prior to all subsampling.

B5.4. Comparability

Comparability is an expression of the confidence with which one data set can be compared with another either between laboratories or within the same laboratory over time.

Analytical data are comparable when similar sampling, analytical methods and QA objectives are used and documented. Within-project data comparability will be ensured in this study because all analyses of a given parameter will be conducted by the same laboratory using consistent personnel and methods. Any data comparisons in this project will be made on surrogate recovery-corrected data. This study will be using a relatively new method for the quantitation of chlorinated bornane/bornenes (Glassmeyer et al., 1999). Therefore, any comparison between the

data in this study and data produced using a different quantitation method should only be done after extensive inter-method comparisons conclude that the methods produce comparable data.

Data comparability within and between laboratories can be assessed by the analyses of standard reference materials as well as participation of the laboratories in analytical round robins. Dr. Swackhamer's laboratory has participated in an international round robin for total toxaphene conducted by Health Canada. This laboratory has also participated in informal sample exchanges among the U of M, the National biological Services/USGS-Ann Arbor and Dr. Hites' Laboratory at Indiana University where total toxaphene agreement was within 20%. Dr. Swackhamer has also participated in two rounds of the Quasimeme Exercises for the analysis of 3 and 4 toxaphene congeners and agreed to within 11% of the true value in solvent and fish extracts.

B5.5. Completeness

Completeness is the percentage of acceptable data needed to validate the study. It is calculated as the number of valid samples divided by the number of samples collected to meet the project objectives, multiplied by 100. Our QA objective for completeness is 90%. Samples passing the MQOs in Table 1 would be considered valid. Invalid samples would be those lost during transport, processing or analysis and those containing unacceptable levels of interferences. Data failing one MQO may be judged valid after review of the data. For example, a sample with low surrogate recovery may be considered valid if the data are consistent with other data and the low recovery can be attributed to a known cause such incorrect spike amount.

B5.6. Blanks

B5.6.a. Field

Field blanks are blank sample matrices that contact the sampling equipment, are transferred to a sample container and are then treated identically to the test samples. They are used to assess contamination from the matrix, sample containers and field equipment involved in sampling. Pre-1900 sediments from deep in each core should contain no measurable chlorinated bornane/bornene or chlordane and will be used as sediment field blanks in this study. One field blank will be analyzed from each sediment core collected. All contaminant concentrations in the blank should be less than or equal to the method detection limit. Sample results will not be corrected for field blank values; analyte concentrations in the samples and blanks will be reported and the blank flagged if greater than the MDL. Field blanks are not applicable to the procedures involved in sediment core dating. True blanks are invariably below the detection limit as background contamination in ^{210}Pb dating is not the problem that it is in trace-contaminant analysis.

B5.6.b. Laboratory

A laboratory procedural blank is run with each set of samples prepared for extraction and is used to assess contamination resulting from laboratory procedures. Laboratory procedural blanks consist of all reagents used in the volumes required for the analyses carried through the entire analytical procedure in the same manner as a sample. Surrogate standards are spiked into the laboratory blanks, identical to samples. All contaminant concentrations should be less than or equal to the method detection limit. Sample results will not be corrected for blank values; analyte concentrations in the samples and blanks will be reported and the blank flagged if greater than the MDL. As discussed in B5.6.a, background contamination is not a problem in ^{210}Pb dating, and blanks are not typically run in this analytical procedure. However upon request, two laboratory blanks will be run during the course of this study.

B5.7. Detectability

Sensitivity can be evaluated at three levels: instrument sensitivity, analytical method sensitivity and overall system sensitivity.

The instrument detection limit (IDL) is the minimum response of the instrument above which you have confidence that the analyte response is greater than the background noise of the instrument. It is determined by running a calibration curve and extrapolating back to the y-intercept. This is done once at the beginning of the project using a minimum of four concentrations in duplicate. It is not necessary to determine this more frequently as the IDL is orders of magnitude below the MDL and is not used in any quantitative way in data review.

Analytical sensitivity is defined as the method detection limit (MDL) which is the minimum concentration above which you have confidence that the analyte was present or not. The MDL for 99% confidence is defined as 3.143 standard deviations of 7 runs of a blank spiked with a very low level of analyte if none is present in the blanks (40 CFR Part 136, Appendix B, Rev.1.11, October 26, 1984). Dr. Swackhamer's laboratory will use field matrix blanks (deep sediment) to determine the MDLs in this project. Spiking the blanks will likely be unnecessary as there is usually sufficient background noise signal in the blanks for this purpose. The target MDLs for chlorinated bornane/bornenes, chlordane and nonachlor in this project are provided in Table 5. These MDLs were determined using the Glassmeyer et al., 1999 method and laboratory procedural blanks. All sample data are examined as to whether the response is below the MDL. Homologs that are below the MDL are considered as zero when summing to determine total chlorinated bornane/bornenes. If any analyte response below the MDL is used in any calculation, data analysis or reporting in this project, it will be flagged to ensure correct interpretation and use of the data. In addition, a set of standards consisting of different ratios of chlordane/nonachlor and toxaphene will be run to demonstrate the level at which chlordane ions are discernable from common ions in technical toxaphene standard.

The overall sensitivity includes influences and uncertainties from the sample collection process and from sample matrices and is the minimum concentration above which you have confidence the analyte was present or not. The system detection limit (SDL) for 99% confidence is defined as three standard deviations of 7 field matrix blanks collected over the course of the project.

Detectable counts in ^{210}Pb dating are ten times the background counts of the detector.

Background counts of 10-14 days are made every 5-6 months on each detector. The lowest count ever measured in an environmental sample by this laboratory was over 2 orders of magnitude greater than the background count of the instrument.

Table 5. Method detection limits for total chlorinated bornane/bornene, homologs, 3 toxaphene congeners (Table A.) and cis- and trans-chlordane and cis- and trans-nonachlor (Table B.) in absolute mass (pg) per sample extract.

A.

Total Cl-bornane/ene	Hexas	Heptas	Octas	Nonas	Decas	Parlar #26	Parlar #50	Parlar #62
1000	120	120	120	200	200	50	50	100

B.

Cis-chlordane	Trans-chlordane	Cis-nonachlor	Trans-nonachlor
164	177	9.3	27.2

B6. Instrument Testing, Inspection and Maintenance

The GC-MS performance is evaluated daily by examining the daily tuning standard octafluoronaphthalene prior to the day's runs and by the evaluation of a toxaphene performance standard included in the day's runs. The instrument is inspected daily for pressures and temperatures. Any deviation from the set pressures and temperatures would require the termination of any runs and a complete evaluation of the instrument. Routine maintenance of the instrument includes 2-3 source cleanings per year, pump oil changes every 3-4 months and clipping of the front of the column and injection port cleanings every 5-6 months. A maintenance agreement with Hewlett-Packard is in place to address any malfunctions and necessary repairs.

The Ortec alpha spectrometer requires only minimum maintenance with no tuning or adjustment during normal operation. Routine maintenance includes daily inspection of isotope peak energies and peak widths relative to established regions of interest. The vacuum pump is serviced every 6-12 months with a change of oil and mist-trap absorbant.

Oven temperature readings are inspected daily. Deviations from set points result in an inspection of the malfunction. All sample processing involving glassware or reagents treated in the oven is halted until the problem is fixed.

Balance performance is evaluated daily by calibration. If a balance cannot be calibrated, the balance will be thoroughly evaluated and sent to the manufacturer for repairs if necessary.

B7. Instrument Calibration and Frequency

The GC-MS is tuned approximately every 2 - 3 weeks. The decision to re-tune the instrument is based on evaluating a daily injection of the performance standard, octafluoronaphthalene. The peak area, shape and electron multiplier setting (sensitivity) are all subjectively evaluated by a trained operator. If re-tuning is judged to be necessary, the instrument is tuned in negative ion mode. If the instrument is shut down for maintenance or repair, it is first tuned in electron impact mode and then tuned in negative ion mode. All tuning observations, runs and maintenance activities are recorded in a dedicated GC-MS logbook.

The Ortec alpha spectrometer is calibrated during the initial setup of the instrument and no additional adjustments are required during normal operation. Detector efficiency is measured by counting a calibrated ^{209}Po source every 2-3 years. Selected samples are exchanged with other ^{210}Pb laboratories several times each year and counted for inter-lab comparison.

Balances are calibrated using standard calibration weights every time the balance is used. This is standard operating procedure and is not recorded separately from the weighing activity.

Pipets and glassware are not calibrated because either we do not need to know the amounts of reagents to an extreme degree of accuracy (e.g. 150 mL of solvent added to a Soxhlet extractor), or the amount that is measured must be very precise but not necessarily very accurate. An example of the latter would be the addition of 50 μL of internal standard solution that is added to every extract using a micropipetter. Because the same pipetter is used for every measurement, the volume added is exactly the same. If the pipetter is replaced, it is calibrated to the previous pipetter by replicate amounts of water that are measured both volumetrically and gravimetrically.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and consumables include solvents, chemicals, paper supplies, computer supplies, and instrument parts. Items where quality lapses would affect the outcome of the project include solvents and chemicals.

Solvents are unpacked on arrival and placed in solvent storage by the lab technician. Neat standards are kept in the freezer after labeling. Other reagents are kept in the chemical storage in the laboratory. Standards are evaluated after dilution to working standards, when they are compared to existing working standards. Concentrations must agree to within 10%. Reagent quality is monitored by the appearance and acceptability of lab procedural blanks.

B9. Data Acquisition Requirements (Non-direct Measurements)

There are no data required from non-measurement sources for the implementation of this project.

B10. Data Management

B10.1. Chlorinated bornane/bornene, chlordane and nonachlor

The sample extracts are injected into the GC-MS, and the resulting ion chromatograms are acquired electronically. All chromatograms will be examined visually for quality of baseline resolution and accuracy of the integration by laboratory personnel, and for spurious peaks that may interfere with the desired signal. After baselines have been reviewed and set, samples will be quantified using the peak areas determined by Hewlett-Packard ChemStation software compared to those of the analytical standards. The areas are transferred electronically into a Microsoft Excel (ver.7.0) spreadsheet, which is pre-formatted to calculate masses, concentrations, quality assurance parameters (e.g. precision, accuracy, surrogate recoveries), and flag non-compliant data. The use of a pre-formatted spreadsheet reduces the potential for calculation errors in data handling. To guard against mistakes and errors in the use of the macros and spreadsheets, a "test" electronic MS datafile will be run through the software with every other batch. All concentrations will be calculated using the internal standard method as follows:

$$\text{mass} = \text{area}_{\text{analyte-ion}} \times \text{RRF} \times [(\text{mass}_{\text{istd}})/(\text{area}_{\text{istd-ion}})]\text{sample}$$

where RRF = relative response factor of the quantitation standard:

$$\text{RRF} = [(\text{mass}_{\text{analyte}})/\text{area}_{\text{analyte-ion}})]/[(\text{mass}_{\text{istd}})/\text{area}_{\text{istd-ion}})]$$

If the internal standard fails QA criteria (Table 1), the sample will be evaluated for errors and flagged.

The analyte concentrations are calculated as:

concentration = (mass of analyte)/(mass of sediment)

The final data are corrected for surrogate recovery as follows:

concentration, corrected = concentration * 100 / % surrogate recovery

All QA data are reviewed for acceptability, and all flagged data are carefully examined to attempt to understand the specific problem in that sample. A narrative will be provided for each data point rejected or used after failing an MQO.

All chromatographic data are backed up on magnetic tape. All Excel files are backed up on either zip or floppy disks. Hard copies of all chromatograms and all spreadsheets are also generated and kept in notebooks.

B10.2. ^{210}Pb dating

Counts of both ^{209}Po and native ^{210}Po are processed using Ortec's Maestro software. Peak areas are integrated using a 1% peak-area cutoff for tails. The recovery of the ^{209}Po spike is used as a correction factor in the quantitation of native ^{210}Po. Raw data sheets are printed out for each analysis. Data are subsequently entered and processed using a proprietary Visual Basic program written by Dr. Daniel Engstrom. All calculations and their derivation are described in Appleby and Oldfield (1978) and Binford (1990).

B10.3. Locational Data

The MPCA will use a Trimble Navigation Pathfinder global positioning system unit (GPS) to determine the position of each sediment core sampling site. The GPS unit is not corrected in real time, so accurate determination of latitude and longitude requires post-operative correction. The uncorrected field GPS coordinates and the associated locational file name will be written into the field notebook immediately upon taking the measurement. The GPS file names will be recorded for later use in the post-processed differential correction. The MPCA data management unit will do this processing.

SECTION C. ASSESSMENT AND OVERSIGHT

C1. Assessment and Response Actions

Dr. Engstrom will collect all sediment cores with assistance from the MPCA. Dr. Engstrom is a recognized expert in this area and will ensure the quality of sample collection. In addition, the MPCA field staff have substantial experience in the collection of sediment cores for contaminant analysis. All field activities as well as any mishaps and deviations from accepted methodologies will be noted in the field notebook by the project manager.

Dr. Swackhamer will monitor project-related laboratory activities at the University of Minnesota. Dr. Engstrom will monitor project-related activities at the St. Croix Watershed Research Station. Any irregularities in staff performance or deviations from lab protocols that affect sample data quality will be corrected and noted in the laboratory book and quarterly reports to MPCA.

Performance and system audits of both field and laboratory activities may be conducted to verify that sampling and analysis are performed in accordance with the procedures established in this QAPP. Potential audits of field and laboratory activities may include two independent parts: internal (MPCA) and external audits (USEPA).

Corrective actions that are analytical in nature include the following: Samples not meeting the MQO for surrogate or matrix spike recoveries will be rerun to rule out artifacts of instrumental analysis. If additional sample is available, a second batch of those samples will be re-extracted and re-analyzed. Data not meeting QA accuracy criteria will be flagged. Drs. Swackhamer and Engstrom will determine if data from their respective laboratories with only one QA flag should be judged valid. A narrative will be provided for each data point rejected or used after failing an MQO.

If the MQOs regarding laboratory and field blanks are exceeded, the samples associated with the set will be evaluated for consistency with previous data sets and the reagents will be checked for purity. If the mass in the blank is <10% of the mass in the associated samples, the sample data will not be flagged. If the data are of questionable quality following these control actions, these samples will be flagged appropriately.

All corrective actions resulting from internal audits will be recorded in laboratory notebooks, and indicated with appropriate QC codes.

All data validation procedures and corrective actions are listed in the MQO Table 1. Following corrective action, project validity will be determined by calculating completeness as described previously.

If data quality is significantly compromised, to an extent where project objectives may not be met, additional sediment cores may be collected depending upon the availability of funding and staff time.

The results of this project may be published, and if so will undergo anonymous outside peer

review by experts in the field.

C2. Reports to Management

The MPCA will provide semi-annual progress reports to the EPA Project Manager and EPA Technical Contact summarizing all progress to date, results of any performance or internal audits, interim data quality assessments and any notable lapses in quality assurance and plans for addressing these problems.

SECTION D. DATA VALIDATION AND USABILITY

D1. Data Review, Validation and Verification Requirements

All data meeting the Measurement Quality Objectives (Table 1) will be considered acceptable and usable by the project. Data having more than one QA qualifier (flag) will not be considered acceptable. Data having one QA qualifier will be carefully examined to determine if the qualifier invalidates the data, or whether the data are still judged acceptable despite the QA qualifier. For example, if the concentration of chlorinated bornane/bornenes in the blank is greater than the MDL, but less than 10% of the sample masses in the associated samples, the data will be accepted without flagging even though the blank for that set will be flagged.

Every chlorinated bornane/bornene /chlordane analytical batch will contain a procedural blank so that laboratory conditions and methods are evaluated on a regular and frequent basis. Procedural blanks with the analyte present greater than the MDL will be considered unacceptable. If these criteria are exceeded, all reagents will be checked before proceeding with additional analyses, and the associated sample sets will be checked against previous ones for self-consistency. If the sample data or reagent purity is questionable, samples will be re-extracted or flagged if no further sample is available. If sample data are consistent with previous data, reagent blanks are acceptable, or the mass of the blank is <10% of the sample mass, then the data will be accepted without flagging. The procedural, field or matrix blanks will not be subtracted from the sample concentrations in any case, but will be reported.

D2. Validation and Verification Methods

The chlorinated bornane/bornene and chlordane data will be acquired and compiled by Dr. Roger Pearson, at the University of Minnesota. Dr. Pearson will also assist with QA review, data validation and data interpretation. Dr. Deborah Swackhamer will have overall responsibility for review of QA/QC data and final decisions on data acceptability. Quarterly summary reports with preliminary data will be provided to the MPCA project manager. The ^{210}Pb data will be acquired and compiled by Ms. Kelly Thommes, Laboratory Coordinator at the St. Croix Watershed Research Station. Dr. Engstrom will have overall responsibility for data review and final decisions regarding data acceptability. Drs. Swackhamer and Engstrom will assist the MPCA with interpretation of the contaminant profiles.

D3. Reconciliation with User Requirements

The overall uncertainty of the data and limitations on data interpretation that this uncertainty poses will be provided to the MPCA by each participating laboratory. The MPCA will include this information in the final report to EPA and to other data users in a peer-reviewed publication. The interpretations of the data will be made within the bounds of that uncertainty and within 90% statistical confidence where applicable.

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APPENDIX B

Summary Report on Sediment Core Dating

St. Louis River Toxaphene Study
Sediment Dating

D.R. Engstrom
June 30, 2001

Lead-210

The three Fond du Lac cores contain low levels of total ^{210}Pb, even in the topmost intervals (3.4-4.2 pCi/g) indicating substantial dilution by high rates of sedimentation in this riverine backwater. Lead-210 activity decreases monotonically downcore to very stable background values (supported ^{210}Pb), ranging from 0.53 to 0.63 pCi/g among the three cores. These stable background values provide a more robust ^{210}Pb chronology than would otherwise be possible with such high rates of sediment deposition and low ^{210}Pb activity. The resulting dates, calculated by the c.r.s. (constant rate of supply) model, confirm the high sediment flux (0.2-0.4 g cm^{-2} yr^{-1}) in recent deposits with substantially lower values in strata that pre-date European settlement. Sedimentation rates are generally similar in cores 1 and 2, and about half that calculated for core-3. Lead-210 dates corresponding to the onset of European settlement (c. 1860-1880) are at 48-52 cm in core-1, 56-60 cm in core-2, and 72-76 cm in core-3). The calculated fluxes of unsupported ^{210}Pb in the three cores (ranging from 0.74-0.94 pCi cm^{-2} yr^{-1}) are higher than that from direct atmospheric ^{210}Pb deposition (0.5 pCi cm^{-2} yr^{-1}) and indicate fluvial transport of ^{210}Pb to the Fond du Lac backwater.

The three cores from West Twin Lake show ^{210}Pb profiles that are typical of small lakes with relatively undisturbed watersheds. Total ^{210}Pb activities are high at the top of the cores (26-31 pCi/g) and decline more-or-less exponentially downcore to stable supported values of 0.63-0.76 pCi/g. The ^{210}Pb chronology modeled from this type of profile is typically very robust. Lead-210 dates corresponding to the onset of logging in this part of northern Minnesota (c. 1900) are at core depths of 42 cm (core-4), 52 cm (core-5) and 46 cm (core-6). All three cores show a consistent increase in sediment accumulation at these depths from pre-1900 rates of ca. 0.01 g cm^{-2} yr^{-1} to rates 2-3x higher in cores 4 and 6 and about 5x in core-5. The higher accumulation rate in core-5 is also reflected in the greater flux of ^{210}Pb to this core site (1.4 pCi cm^{-2} yr^{-1}) as compared to the other two (0.81-0.87 pCi cm^{-2} yr^{-1}), and indicates intense sediment focusing to the deep-water location where core-5 was collected.

Loss-on-Ignition

The organic content of the Fond du Lac cores is in the range of 10% or less except at the base of core-2 where fibrous peat (with upwards of 50% organic matter) was encountered. Highly inorganic sediments are typical of large river systems dominated by erosional transport of suspended silts and clays. The presence of peat at the bottom of core-2 suggests that this core-site (and perhaps the entire embayment) was at one time isolated from direct riverine inputs. Organic content increases upcore in the profiles from sites 1 and 3 at depths generally

corresponding to the time of European settlement (1860-1880) -- 52 cm in core-1 and 64 cm in core-3.

Organic content in the West Twin cores ranges from 50-60% with upcore declines clearly evident at 24 cm in core-4, 52 cm in core-5 and 35 cm in core-6. Dates corresponding to these changes in lithology are c. 1945 in cores 4 and 6 and 1900 in core-5, indicating different core-specific responses to land-use changes in the watershed. The increase in inorganic content in core-5 corresponds to a rise in sedimentation rate and indicates increased erosion associated with logging at the turn of the century. The LOI changes in cores 4 and 6, on the other hand, may be an erosional signal associated with residential lake-shore development following WW II.

Cesium-137

Radio-cesium profiles for the three Fond du Lac cores show clear peaks that provide independent dating markers based on the known history of atmospheric nuclear testing. These peaks -- at 26-28 cm in core-1, 22-24 cm in core-2, and 24-26 cm in core-3 --correspond to ^{210}Pb dates of 1958-1961, 1961-65, and 1967-70, in cores 1 through 3 respectively. Peak fallout of ^{137}Cs is placed at about 1963, which fits exactly the ^{210}Pb chronology for core-2, but is slightly younger than the corresponding ^{210}Pb dates in core-1 and slightly older than the ^{210}Pb dates in core-3. However, the ^{210}Pb and ^{137}Cs results are remarkably close given the uncertainty of ^{210}Pb dating in this type of sedimentary environment, and differences are within 2 sigma of the ^{210}Pb dates.

Pollen

Pollen profiles constructed for the three Fond du Lac cores reveal a clear stratigraphic change from a pre-settlement assemblage dominated by pine (*Pinus*), birch (*Betula*), and grasses (Poaceae) to one with dramatically increased percentages of grass and ragweed (*Ambrosia*) and a sharp reduction in pine and birch pollen. This transition represents the onset of European settlement and logging of local pine forests along the lower St. Louis River. The exact timing of this settlement horizon" is difficult to fix for a watershed the size of that contributing to the Fond du Lac site, but is most likely associated with commercial logging and early growth of the city of Duluth (c. 1860-1880). The corresponding depths and ^{210}Pb dates are 46-48 cm (1883-1892) in core-1, 56-60 cm (1861-1887) in core-2, and 60-64 cm (1911-1921) in core-3. The palynological results indicate that the ^{210}Pb chronology for core-3 is seriously in error for these older dates, but that the ^{210}Pb results for cores 1 and 2 are reliable.

APPENDIX C

Loss on Ignition Data

St. Louis River Sediment Core #1: Loss on Ignition Data

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Wet (g/cc)	Dry (g/cc)	% Organic	% CaCO3	% Inorganic
0	2	1.13	0.216	10.81	3.96	85.2
2	4	1.17	0.299	9.77	3.74	86.5
4	6	1.21	0.365	9.10	3.75	87.1
6	8	1.24	0.413	8.86	3.64	87.5
8	10	1.27	0.462	8.72	3.49	87.8
10	12	1.29	0.497	8.58	3.32	88.1
12	14	1.29	0.501	8.53	3.32	88.1
14	16	1.32	0.551	8.03	3.28	88.7
16	18	1.34	0.573	7.97	3.26	88.8
18	20	1.36	0.605	7.81	3.07	89.1
20	22	1.35	0.590	8.48	3.11	88.4
22	24	1.36	0.606	8.08	2.99	88.9
24	26	1.35	0.598	8.39	3.01	88.6
26	28	1.36	0.605	8.71	3.43	87.9
28	30	1.32	0.546	9.80	3.77	86.4
30	32	1.31	0.530	10.04	3.63	86.3
32	34	1.33	0.563	9.06	3.52	87.4
34	36	1.33	0.563	9.15	3.43	87.4
36	38	1.35	0.597	8.67	3.20	88.1
38	40	1.35	0.595	9.09	3.27	87.6
40	42	1.29	0.494	10.14	4.23	85.6
42	44	1.27	0.468	10.57	3.89	85.5
44	46	1.29	0.496	10.55	3.14	86.3
46	48	1.19	0.347	21.68	3.23	75.1
48	52	1.21	0.375	19.29	3.25	77.5
52	56	1.39	0.659	5.94	2.67	91.4
56	60	1.37	0.614	6.35	2.52	91.1
60	64	1.38	0.633	6.52	2.36	91.1
64	68	1.46	0.765	5.92	2.05	92.0
68	72	1.47	0.785	6.17	1.96	91.9
72	76	1.51	0.848	5.37	2.09	92.5
76	80	1.54	0.905	4.73	2.07	93.2
80	84	1.52	0.869	4.88	2.34	92.8
84	88	1.52	0.861	5.00	2.50	92.5
88	92	1.56	0.929	4.49	2.49	93.0
92	96	1.53	0.888	4.92	2.37	92.7
96	100	1.52	0.865	5.21	2.19	92.6
100	104	1.45	0.758	5.99	2.38	91.6
104	108	1.45	0.753	5.98	2.43	91.6
108	112	1.42	0.709	6.30	2.41	91.3

St. Louis River Sediment Core #2 Loss on Ignition Data

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Wet (g/cc)	Dry (g/cc)	% Organic	% CaCO3	% Inorganic
0	2	1.08	0.137	14.32	4.69	81.0
2	4	1.12	0.205	12.20	6.41	81.4
4	6	1.13	0.217	11.86	4.47	83.7
6	8	1.16	0.282	11.08	4.14	84.8
8	10	1.19	0.335	10.69	3.99	85.3
10	12	1.21	0.357	10.60	3.80	85.6
12	14	1.22	0.372	10.52	3.88	85.6
14	16	1.22	0.386	10.37	3.64	86.0
16	18	1.25	0.436	10.44	3.83	85.7
18	20	1.27	0.469	10.60	3.72	85.7
20	22	1.26	0.452	10.91	3.85	85.2
22	24	1.26	0.451	11.08	4.00	84.9
24	26	1.26	0.456	11.45	4.19	84.4
26	28	1.26	0.458	11.54	4.27	84.2
28	30	1.28	0.488	10.68	4.09	85.2
30	32	1.27	0.465	11.55	3.94	84.5
32	34	1.27	0.460	11.68	4.00	84.3
34	36	1.23	0.404	12.77	4.52	82.7
36	38	1.24	0.416	12.93	4.25	82.8
38	40	1.25	0.434	14.29	3.84	81.9
40	42	1.26	0.450	13.25	3.94	82.8
42	44	1.25	0.438	11.58	3.98	84.4
44	46	1.30	0.508	10.53	3.41	86.1
46	48	1.31	0.540	10.65	3.10	86.3
48	52	1.32	0.546	10.79	2.76	86.5
52	56	1.31	0.535	10.54	2.93	86.5
56	60	1.22	0.401	16.55	3.16	80.3
60	64	1.24	0.412	12.41	3.02	84.6
64	68	1.21	0.370	14.69	2.97	82.3
68	72	1.17	0.320	21.81	3.05	75.1
72	76	1.17	0.326	24.49	2.85	72.7
76	80	1.15	0.288	28.82	2.71	68.5
80	84	1.10	0.202	43.92	2.76	53.3
84	88	1.09	0.191	47.60	2.81	49.6
88	92	1.08	0.181	48.85	2.95	48.2

St. Louis River Sediment Core #3 Loss on Ignition Data

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Wet (g/cc)	Dry (g/cc)	% Organic	% CaCO3	% Inorganic
0	2	1.13	0.223	12.18	3.38	84.4
2	4	1.18	0.309	9.96	3.23	86.8
4	6	1.24	0.400	8.50	3.13	88.4
6	8	1.26	0.447	8.50	3.64	87.9
8	10	1.31	0.520	7.94	3.96	88.1
10	12	1.31	0.523	8.23	3.44	88.3
12	14	1.34	0.584	7.91	3.35	88.7
14	16	1.37	0.623	7.61	3.08	89.3
16	18	1.37	0.635	7.79	3.16	89.0
18	20	1.36	0.606	8.43	3.12	88.4
20	22	1.37	0.623	8.48	3.05	88.5
22	24	1.37	0.624	8.61	3.02	88.4
24	26	1.35	0.603	9.08	3.23	87.7
26	28	1.35	0.592	9.33	3.13	87.5
28	30	1.36	0.614	9.06	3.14	87.8
30	32	1.37	0.625	9.18	2.91	87.9
32	34	1.38	0.649	8.60	2.89	88.5
34	36	1.30	0.524	10.86	3.50	85.6
36	38	1.28	0.477	11.95	3.55	84.5
38	40	1.28	0.489	11.34	3.53	85.1
40	42	1.27	0.473	11.65	3.76	84.6
42	44	1.30	0.509	10.40	3.53	86.1
44	46	1.31	0.527	9.79	3.43	86.8
46	48	1.29	0.504	10.17	3.63	86.2
48	52	1.33	0.560	9.96	2.84	87.2
52	56	1.37	0.639	8.89	2.44	88.7
56	60	1.35	0.599	9.61	2.49	87.9
60	64	1.37	0.627	8.60	2.42	89.0
64	68	1.36	0.602	7.35	2.40	90.3
68	72	1.39	0.649	6.54	2.39	91.1
72	76	1.37	0.617	7.13	2.47	90.4
76	80	1.38	0.641	7.21	2.42	90.4
80	84	1.44	0.744	6.40	2.05	91.5
84	88	1.57	0.946	5.01	1.59	93.4
88	92	1.62	1.036	4.42	1.61	94.0
92	96	1.57	0.952	4.87	1.77	93.4
96	100	1.60	1.005	4.37	1.78	93.8
100	104	1.62	1.025	4.35	1.75	93.9
104	108	1.65	1.084	4.07	1.66	94.3
108	112	1.58	0.963	4.94	1.57	93.5

West Twin Lake Sediment Core #4 Loss on Ignition Data

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Wet (g/cc)	Dry (g/cc)	% Organic	% CaCO3	% Inorganic
0	2	1.02	0.037	55.41	5.17	39.4
2	4	1.02	0.042	54.36	5.28	40.4
4	6	1.02	0.043	53.60	5.46	40.9
6	8	1.02	0.039	53.15	5.66	41.2
8	10	1.02	0.041	52.69	5.98	41.3
10	12	1.02	0.044	52.06	5.48	42.5
12	14	1.02	0.049	52.19	4.98	42.8
14	16	1.02	0.052	50.94	5.78	43.3
16	18	1.02	0.055	50.29	5.94	43.8
18	20	1.03	0.056	50.43	5.42	44.2
20	22	1.03	0.060	51.09	2.98	45.9
22	24	1.03	0.062	53.72	2.97	43.3
24	26	1.02	0.057	56.37	3.64	40.0
26	28	1.02	0.057	58.89	2.08	39.0
28	30	1.02	0.056	61.12	3.46	35.4
30	32	1.02	0.056	59.74	4.41	35.8
32	34	1.02	0.058	56.75	4.43	38.8
34	36	1.02	0.056	57.20	4.14	38.7
36	38	1.02	0.053	58.85	4.54	36.6
38	40	1.02	0.053	59.44	4.33	36.2
40	42	1.02	0.053	59.75	4.44	35.8
42	44	1.02	0.051	60.85	3.55	35.6
44	46	1.02	0.051	61.40		-271.8
46	48	1.02	0.052	61.47	3.73	34.8
48	52	1.02	0.052	61.98	3.08	34.9
52	56	1.02	0.054	61.87	2.92	35.2
56	60	1.02	0.052	63.12	2.74	34.1
60	64	1.02	0.045	62.75	2.27	35.0
64	68	1.02	0.051	62.18	2.40	35.4
68	72	1.01	0.035	61.85	1.25	36.9
72	76	1.03	0.073	61.43	2.71	35.9
76	80	1.02	0.052	61.18	2.48	36.3
80	84	1.02	0.053	59.96	3.47	36.6
84	88	1.02	0.053	59.43	3.50	37.1
88	92	1.02	0.056	58.49	3.46	38.1
92	96	1.02	0.055	57.92	2.80	39.3
96	100	1.02	0.058	57.12	3.16	39.7
100	104	1.03	0.061	58.12	3.02	38.9
104	108	1.02	0.055	61.99	3.36	34.7
108	112	1.02	0.058	61.12	2.98	35.9

West Twin Lake Sediment Core #5 Loss on Ignition Data

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Wet (g/cc)	Dry (g/cc)	% Organic	% CaCO3	% Inorg.
0	2	1.02	0.033	51.15	6.81	42.0
2	4	1.02	0.039	51.43	5.95	42.6
4	6	1.02	0.042	51.29	5.61	43.1
6	8	1.02	0.045	51.57	6.07	42.4
8	10	1.02	0.046	51.37	6.01	42.6
10	12	1.02	0.047	51.66	6.40	41.9
12	14	1.02	0.049	51.61	6.80	41.6
14	16	1.02	0.050	51.10	6.12	42.8
16	18	1.02	0.052	50.84	6.14	43.0
18	20	1.03	0.057	50.60	5.91	43.5
20	22	1.03	0.061	50.74	5.44	43.8
22	24	1.03	0.062	50.66	5.48	43.9
24	26	1.03	0.062	50.79	5.70	43.5
26	28	1.03	0.064	50.52	5.23	44.2
28	30	1.03	0.064	50.97	5.32	43.7
30	32	1.03	0.064	51.29	5.14	43.6
32	34	1.03	0.064	51.20	4.89	43.9
34	36	1.03	0.064	51.70	5.12	43.2
36	38	1.03	0.065	51.97	4.97	43.1
38	40	1.03	0.065	52.10	4.89	43.0
40	42	1.03	0.065	51.67	5.03	43.3
42	44	1.03	0.067	51.77	5.29	42.9
44	46	1.03	0.068	51.79	4.73	43.5
46	48	1.03	0.069	51.55	4.95	43.5
48	52	1.03	0.071	51.51	4.82	43.7
52	56	1.03	0.059	56.77	4.55	38.7
56	60	1.02	0.057	59.04	4.20	36.8
60	64	1.02	0.055	59.55	4.00	36.4
64	68	1.02	0.055	60.16	3.76	36.1
68	72	1.02	0.055	60.91	3.76	35.3
72	76	1.02	0.055	61.57	3.45	35.0
76	80	1.02	0.054	60.33	3.50	36.2
80	84	1.02	0.055	59.71	3.78	36.5
84	88	1.02	0.056	58.01	4.20	37.8
88	92	1.02	0.057	57.46	3.83	38.7
92	96	1.02	0.058	56.39	3.77	39.8
96	100	1.03	0.059	55.95	3.66	40.4
100	104	1.03	0.062	56.25	3.98	39.8
104	108	1.03	0.059	55.75	4.19	40.1
108	112	1.03	0.061	55.60	4.28	40.1

West Twin Lake Sediment Core #6 Loss on Ignition Data

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Wet (g/cc)	Dry (g/cc)	% Organic	% CaCO3	% Inorg.
0	2	1.01	0.033	50.48	5.77	43.8
2	4	1.02	0.037	50.34	5.53	44.1
4	6	1.02	0.040	50.43	5.52	44.0
6	8	1.02	0.044	50.25	5.62	44.1
8	10	1.02	0.045	50.46	5.92	43.6
10	12	1.02	0.048	50.19	5.62	44.2
12	14	1.02	0.045	50.19	5.74	44.1
14	16	1.02	0.046	50.15	5.59	44.3
16	18	1.02	0.048	49.98	5.35	44.7
18	20	1.02	0.052	49.89	5.06	45.1
20	22	1.02	0.055	49.47	4.93	45.6
22	24	1.03	0.058	49.39	4.95	45.7
24	26	1.03	0.060	49.40	5.05	45.5
26	28	1.03	0.061	49.45	4.67	45.9
28	30	1.03	0.061	49.81	4.73	45.5
30	32	1.03	0.061	50.15	4.75	45.1
32	34	1.03	0.061	51.81	4.61	43.6
34	36	1.02	0.054	55.44	4.63	39.9
36	38	1.02	0.051	56.89	4.63	38.5
38	40	1.02	0.052	56.88	4.48	38.6
40	42	1.02	0.052	56.53	3.31	40.2
42	44	1.02	0.055	56.32	4.28	39.4
44	46	1.02	0.054	57.14	4.01	38.8
46	48	1.02	0.053	57.61	4.24	38.1
48	52	1.02	0.052	58.52	4.23	37.2
52	56	1.02	0.053	58.86	3.84	37.3
56	60	1.02	0.053	58.35	3.52	38.1
60	64	1.02	0.053	59.17	3.38	37.5
64	68	1.02	0.051	60.09	3.61	36.3
68	72	1.02	0.051	59.88	3.25	36.9
72	76	1.02	0.051	58.25	3.35	38.4
76	80	1.02	0.054	57.45	3.99	38.6
80	84	1.02	0.050	57.41	3.97	38.6
84	88	1.02	0.052	56.82	4.12	39.1
88	92	1.02	0.051	55.89	3.82	40.3
92	96	1.02	0.055	55.75	3.80	40.5
96	100	1.02	0.057	54.25	3.91	41.8
100	104	1.02	0.056	54.43	4.20	41.4
104	108	1.02	0.055	55.95	4.19	39.9
108	112	1.03	0.059	56.54	4.29	39.2

APPENDIX D

^{210}Pb and Sedimentation Rates

St. Louis River Sediment Core #1 - Dating and Sedimentation Rates

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Cumulative Dry Mass (g/cm2)	Unsupported Activity (pCi/g)	Error of Unsupported Activity (± s.d.)	Cumulative Activity below Section (pCi/cm2)	Age at Base of Section (Yr)	Error of Age (±s.d.)	Date A.D.	Sediment Accumulation rate (g/cm2/yr)	Error of Sediment Accumulation (±s.d.)
0	2	0.4	3.61	0.081	24.0	2.0	1.61	1997.5	0.214	0.009
2	4	1.0	2.81	0.072	22.3	4.4	1.67	1995.1	0.256	0.012
4	6	1.8	2.34	0.059	20.6	6.9	1.75	1992.6	0.285	0.014
6	8	2.6	1.95	0.044	19.0	9.5	1.84	1989.9	0.315	0.015
12	14	5.4	1.46	0.037	14.4	18.4	1.99	1981.1	0.322	0.018
18	20	8.8	0.87	0.051	10.8	27.6	1.4	1971.9	0.407	0.025
24	26	12.4	0.85	0.047	7.7	38.3	1.58	1961.2	0.301	0.019
30	32	15.8	0.72	0.048	5.2	51.0	1.68	1948.4	0.242	0.018
32	34	16.9	0.66	0.033	4.5	56.0	1.83	1943.5	0.227	0.014
34	36	18.0	0.61	0.032	3.8	61.4	2.02	1938.1	0.209	0.014
36	38	19.2	0.48	0.040	3.2	66.7	2.24	1932.8	0.223	0.021
40	42	21.3	0.73	0.035	1.8	84.9	2.56	1914.6	0.092	0.007
42	44	22.2	0.68	0.044	1.2	98.7	3.56	1900.8	0.068	0.007
44	46	23.2	0.30	0.028	0.9	107.9	4.53	1891.6	0.108	0.016
46	48	23.9	0.30	0.033	0.7	116.5	5.74	1883	0.081	0.015
48	52	25.4	0.33	0.026	0.2	157.4	19.08	1842.1	0.037	0.012
52	56	28.0	0.05	0.025	0.1	190.0	42.67	1809.5	0.081	0.073

Supported Pb-210: 0.5952 ± 0.0153 pCi/gCum. Unsup. Pb-210: 25.5418 pCi/cm2
Number of Supported Samples: 4Unsup. Pb-210 Flux: 0.8145 pCi/cm2 yr

St. Louis River Sediment Core #2 - Dating and Sedimentation Rates

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Cumulative Dry Mass (g/cm2)	Unsupported Activity (pCi/g)	Error of Unsupported Activity (± s.d.)	Cumulative Activity below Section (pCi/cm2)	Age at Base of Section (Yr)	Error of Age (±s.d.)	Date A.D.	Sediment Accumulation rate (g/cm2/yr)	Error of Sediment Accumulation (±s.d.)
0	2	0.3	3.40	0.077	22.3	1.3	0.81	1998.2	0.209	0.006
4	6	1.1	3.17	0.135	19.8	5.2	0.86	1994.3	0.201	0.009
6	8	1.6	2.61	0.047	18.3	7.7	0.9	1991.8	0.227	0.006
10	12	3.0	2.47	0.109	14.9	14.3	1	1985.2	0.199	0.010
12	14	3.7	2.06	0.040	13.4	17.8	1.08	1981.7	0.213	0.007
16	18	5.4	1.71	0.077	10.4	26.0	1.22	1973.5	0.202	0.011
18	20	6.3	1.23	0.031	9.2	29.7	1.34	1969.8	0.248	0.011
22	24	8.2	1.27	0.075	6.9	38.9	1.67	1960.6	0.184	0.013
24	26	9.1	1.03	0.027	6.0	43.6	1.9	1955.9	0.195	0.011
28	30	11.0	0.74	0.053	4.4	53.2	2.28	1946.2	0.201	0.018
30	32	11.9	0.62	0.027	3.9	57.7	2.59	1941.8	0.208	0.017
34	36	13.6	0.67	0.047	2.8	68.5	3.53	1931	0.141	0.017
36	38	14.4	0.43	0.024	2.4	72.9	4.04	1926.6	0.186	0.024
40	42	16.2	0.24	0.028	1.9	80.5	4.86	1919	0.259	0.047
42	44	17.1	0.28	0.030	1.6	85.0	5.56	1914.5	0.196	0.037
46	48	19.1	0.13	0.030	1.3	92.2	6.63	1907.3	0.340	0.102
48	52	21.3	0.13	0.027	1.0	99.8	8.18	1899.7	0.289	0.086
56	60	24.8	0.24	0.032	0.3	138.6	24	1860.9	0.062	0.032
64	68	27.8	0.04	0.019	0.0	204.2	139.06	1795.3	0.049	0.140

Supported Pb-210: 0.6352 ± 0.0127 pCi/gCum. Unsup. Pb-210: 23.2435 pCi/cm2
Number of Supported Samples: 3Unsup. Pb-210 Flux: 0.7427 pCi/cm2 yr

St. Louis River Sediment Core #3 - Dating and Sedimentation Rates

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Cumulative Dry Mass (g/cm2)	Unsupported Activity (pCi/g)	Error of Unsupported Activity (± s.d.)	Cumulative Activity below Section (pCi/cm2)	Age at Base of Section (Yr)	Error of Age (±s.d.)	Date A.D.	Sediment Accumulation rate (g/cm2/yr)	Error of Sediment Accumulation (±s.d.)
0	2	0.4	2.87	0.117	28.3	1.4	1.62	1998.1	0.313	0.017
4	6	1.9	2.12	0.104	25.0	5.3	1.7	1994.2	0.380	0.023
6	8	2.8	1.97	0.054	23.3	7.7	1.78	1991.8	0.382	0.019
10	12	4.8	1.58	0.075	19.9	12.7	1.93	1986.8	0.407	0.027
12	14	6.0	1.40	0.047	18.2	15.5	2.05	1984	0.422	0.025
16	18	8.4	1.09	0.060	15.4	21.0	2.28	1978.5	0.459	0.036
18	20	9.7	0.96	0.043	14.2	23.5	2.42	1975.9	0.480	0.037
24	26	13.3	0.94	0.041	10.8	32.4	3.03	1967.1	0.375	0.035
28	30	15.7	0.63	0.051	9.0	38.0	3.45	1961.5	0.466	0.058
30	32	17.0	0.47	0.035	8.5	40.2	3.66	1959.3	0.580	0.074
36	38	20.1	0.63	0.038	6.6	48.0	4.48	1951.5	0.340	0.048
40	42	22.0	0.53	0.048	5.6	53.5	5.26	1946	0.343	0.060
42	44	23.0	0.37	0.036	5.2	55.8	5.62	1943.7	0.451	0.086
48	52	27.4	0.28	0.032	3.9	65.2	7.38	1934.3	0.472	0.112
60	64	34.7	0.28	0.031	1.9	88.8	15.03	1910.7	0.244	0.100
64	68	37.1	0.21	0.039	1.3	99.1	20.55	1900.4	0.234	0.133
72	76	42.0	0.12	0.028	0.6	123.1	42.81	1876.3	0.197	0.220

Supported Pb-210: 0.5389 ± 0.0251 pCi/gCum. Unsup. Pb-210: 29.536 pCi/cm2
Number of Supported Samples: 4Unsup. Pb-210 Flux: 0.9442 pCi/cm2 yr

West Twin Lake Sediment Core #4 - Dating and Sedimentation Rates.

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Cumulative Dry Mass (g/cm2)	Unsupported Activity (pCi/g)	Error of Unsupported Activity (± s.d.)	Cumulative Activity below Section (pCi/cm2)	Age at Base of Section (Yr)	Error of Age (±s.d.)	Date A.D.	Sediment Accumulation rate (g/cm2/yr)	Error of Sediment Accumulation (±s.d.)
0	2	0.07	27.07	0.79	23.0	2.7	0.49	1996.8	0.028	0.001
4	6	0.24	25.40	0.86	18.7	9.3	0.51	1990.2	0.024	0.001
6	8	0.32	22.09	0.84	17.0	12.4	0.53	1987.1	0.025	0.001
8	10	0.40	20.52	0.65	15.3	15.8	0.56	1983.7	0.025	0.001
12	14	0.59	18.44	0.61	11.7	24.3	0.59	1975.2	0.021	0.001
14	16	0.69	15.31	0.52	10.1	29.0	0.63	1970.5	0.022	0.001
16	18	0.80	15.22	0.50	8.5	34.8	0.69	1964.7	0.019	0.001
18	20	0.92	13.57	0.50	6.9	41.2	0.76	1958.3	0.018	0.001
20	22	1.04	11.17	0.29	5.6	48.1	0.89	1951.4	0.017	0.001
22	24	1.16	7.20	0.32	4.7	53.6	0.99	1945.9	0.022	0.001
24	26	1.27	4.64	0.17	4.2	57.4	1.10	1942.1	0.030	0.001
26	28	1.39	4.35	0.15	3.7	61.4	1.22	1938.0	0.028	0.001
28	30	1.50	2.99	0.14	3.4	64.5	1.33	1935.0	0.037	0.002
32	34	1.73	3.76	0.14	2.5	73.4	1.61	1926.1	0.023	0.001
36	38	1.94	2.87	0.13	1.9	83.3	1.97	1916.2	0.022	0.002
40	42	2.16	2.73	0.12	1.3	95.4	2.81	1904.1	0.016	0.001
44	46	2.36	2.40	0.13	0.8	111.5	4.52	1887.9	0.012	0.002
46	48	2.47	2.44	0.13	0.5	124.3	6.65	1875.2	0.008	0.001
48	52	2.67	1.26	0.12	0.3	146.9	13.11	1852.5	0.009	0.003
52	56	2.89	0.50	0.11	0.1	164.4	21.96	1835.1	0.013	0.007
56	60	3.10	0.32	0.11	0.1	183.1	38.25	1816.4	0.011	0.011

Supported Pb-210: 0.6274 ± 0.1061 pCi/gCum. Unsup. Pb-210: 25.0058 pCi/cm2
Number of Supported Samples: 2Unsup. Pb-210 Flux: 0.8094 pCi/cm2 yr

West Twin Lake Sediment Core #5 - Dating and Sedimentation Rates.

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Cumulative Dry Mass (g/cm2)	Unsupported Activity (pCi/g)	Error of Unsupported Activity (± s.d.)	Cumulative Activity below Section (pCi/cm2)	Age at Base of Section (Yr)	Error of Age (±s.d.)	Date A.D.	Sediment Accumulation rate (g/cm2/yr)	Error of Sediment Accumulation (±s.d.)
0	2	0.07	30.49	0.86	40.9	1.6	0.51	1997.9	0.043	0.001
4	6	0.23	23.60	0.81	36.8	4.9	0.49	1994.6	0.050	0.002
6	8	0.32	20.34	0.79	35.0	6.5	0.49	1992.9	0.055	0.002
8	10	0.41	10.22	0.26	34.1	7.4	0.50	1992.1	0.105	0.003
10	12	0.50	15.07	0.50	32.6	8.8	0.51	1990.7	0.069	0.002
12	14	0.60	13.65	0.49	31.3	10.1	0.52	1989.4	0.073	0.003
16	18	0.81	14.88	0.27	28.3	13.4	0.54	1986.1	0.061	0.001
24	26	1.27	13.73	0.34	21.7	21.8	0.56	1977.7	0.051	0.001
32	34	1.77	12.46	0.27	15.2	33.2	0.47	1966.3	0.040	0.001
36	38	2.03	11.28	0.21	12.3	40.2	0.47	1959.3	0.036	0.001
40	42	2.29	11.38	0.23	9.3	49.0	0.53	1950.5	0.028	0.001
44	46	2.56	10.54	0.20	6.4	60.9	0.58	1938.6	0.021	0.000
48	52	2.98	10.55	0.22	2.0	98.5	1.11	1901.0	0.010	0.000
52	56	3.22	3.96	0.13	1.1	118.9	1.77	1880.6	0.012	0.001
56	60	3.45	1.90	0.10	0.6	135.9	2.71	1863.6	0.014	0.001
60	64	3.67	1.16	0.07	0.4	152.8	4.34	1846.7	0.013	0.002
64	68	3.89	0.73	0.07	0.2	171.4	7.33	1828.0	0.012	0.002
68	72	4.11	0.42	0.07	0.1	190.1	12.44	1809.4	0.012	0.004
72	76	4.32	0.25	0.07	0.1	211.2	22.75	1788.3	0.010	0.006

Supported Pb-210: 0.7605 ± 0.0557 pCi/gCum. Unsup. Pb-210: 42.898 pCi/cm2
Number of Supported Samples: 2Unsup. Pb-210 Flux: 1.3898 pCi/cm2 yr

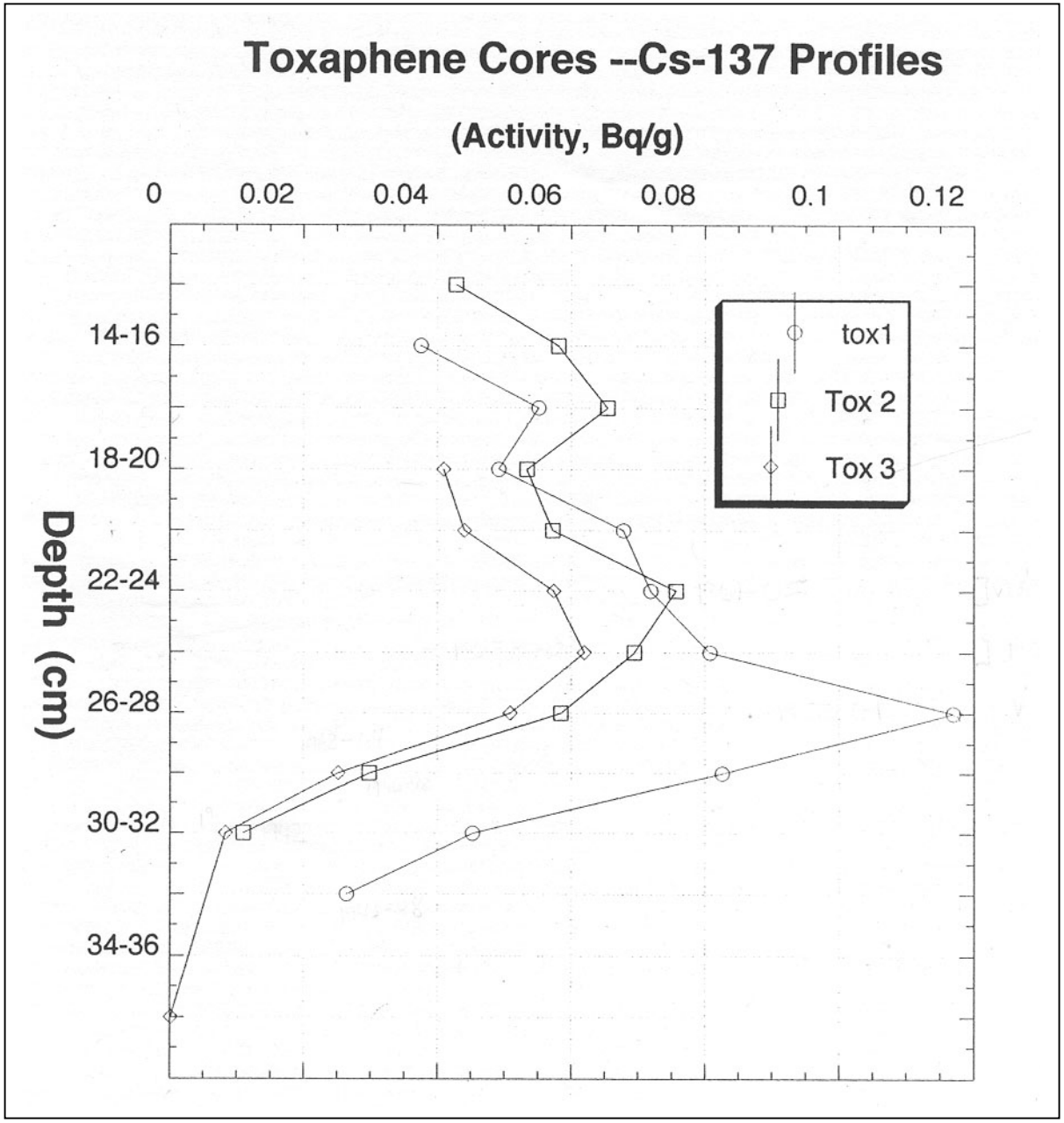
West Twin Lake Sediment Core #6 - Dating and Sedimentation Rates

Depth of Section at Top (cm)	Depth of Section at Base (cm)	Cumulative Dry Mass (g/cm2)	Unsupported Activity (pCi/g)	Error of Unsupported Activity (± s.d.)	Cumulative Activity below Section (pCi/cm2)	Age at Base of Section (Yr)	Error of Age (±s.d.)	Date A.D.	Sediment Accumulation rate (g/cm2/yr)	Error of Sediment Accumulation (±s.d.)
0	2	0.07	25.83	0.77	25.1	2.1	0.74	1997.4	0.031	0.001
4	6	0.22	22.05	0.62	21.6	7.0	0.77	1992.5	0.032	0.001
6	8	0.31	19.68	0.68	19.9	9.6	0.81	1989.9	0.033	0.001
8	10	0.40	16.06	0.45	18.4	12.0	0.84	1987.5	0.037	0.001
12	14	0.57	15.69	0.44	15.6	17.4	0.94	1982.1	0.032	0.001
14	16	0.67	13.20	0.52	14.4	20.0	0.99	1979.5	0.035	0.002
16	18	0.76	12.20	0.41	13.2	22.7	1.05	1976.8	0.035	0.001
18	20	0.87	11.73	0.45	12.0	25.8	1.12	1973.7	0.033	0.002
20	22	0.98	12.40	0.41	10.6	29.7	1.23	1969.8	0.028	0.001
22	24	1.09	12.00	0.24	9.2	34.2	1.39	1965.3	0.026	0.001
24	26	1.21	12.18	0.38	7.8	39.8	1.60	1959.7	0.022	0.001
28	30	1.46	10.66	0.34	5.1	53.5	2.29	1946.0	0.017	0.001
32	34	1.70	6.43	0.23	3.3	67.5	2.48	1932.0	0.018	0.001
34	36	1.81	3.30	0.16	2.9	71.2	2.77	1928.3	0.029	0.003
36	38	1.91	3.27	0.18	2.6	75.1	3.11	1924.4	0.026	0.003
40	42	2.12	3.20	0.15	1.9	84.7	4.15	1914.7	0.020	0.003
44	46	2.33	2.99	0.14	1.3	98.1	6.23	1901.4	0.015	0.003
48	52	2.65	2.24	0.14	0.5	126.9	14.90	1872.6	0.010	0.003
56	60	3.07	0.54	0.13	0.1	167.3	37.04	1832.1	0.011	0.010

Supported Pb-210: 0.6549 ± 0.124 pCi/gCum. Unsup. Pb-210: 26.7944 pCi/cm2
Number of Supported Samples: 2Unsup. Pb-210 Flux: 0.8684 pCi/cm2 yr

APPENDIX E

^{137}Cs Data


Toxaphene Cores --Cs-137 Profiles
(Activity, Bq/g)
0
0.02
0.04
0.06
0.08
0.1
0.12
Depth (cm)
14-16
18-20
22-24
26-28
30-32
34-36
tox1
Tox 2
Tox 3

^{137}Cs data for St. Louis River sediment cores.

Depth (cm)	Core #1 Cs-137 (bq/g)	Std dev tox 1	Core #2 Cs-137 (bq/g)	Std dev Tox 2	Core #3 Cs-137 (bq/g)	Std dev Tox 3
12-14			0.0428	0.005		
14-16	0.0376	0.00376	0.0581	0.0051		
16-18	0.0552	0.0012	0.0655	0.0032		
18-20	0.0492	0.0061	0.0534	0.0041	0.041	0.00211
20-22	0.0679	0.0032	0.0573	0.0021	0.0441	0.00215
22-24	0.0719	0.0069	0.0757	0.0045	0.0574	0.00671
24-26	0.0808	0.0034	0.0695	0.0037	0.062	0.00378
26-28	0.117	0.0087	0.0585	0.00123	0.0509	0.00371
28-30	0.0826	0.0043	0.0298	0.0045	0.02522	0.00245
30-32	0.0453	0.0012	0.01105	0.0021	0.00837	0.00099
32-34	0.0265	0.0035				
34-36						
36-38					0.000128	0.000055

Toxaphene Cores, St. Louis River, Minnesota
Run Febuary/March 2000,
St. Croix Watershed Research Station
Shawn Schottler, Detectors 1 and 2.
All activities in Bq/g
(multiply by 27.02 to convert to pCi/g)

APPENDIX F

Pollen Data

St. Louis River Core #1

Number of samples 6

Number of taxa 21

Depth	40	44	46	48	52	56
Sample #	40-42	44-46	46-48	48-52	52-56	56-60
Pinus dip.	2	3	6	3	5	4
Pinus hap	2	3	7	13	8	10
Pinus undiff	15	12	13	10	17	18
Total Pinus	19	18	27	26	30	32
Picea glauca	1	0	2	1	1	1
Larix	0	0	0	0	2	1
Cupressaceae	1	1	2	4	2	1
Tsuga	0	1	0	0	0	2
Quercus	3	2	1	3	2	3
Betula	5	11	10	19	18	17
Alnus rugosa	5	7	4	4	7	5
Salix	2	1	2	0	1	1
Populus	1	0	1	1	1	0
Poaceae	30	36	32	33	22	24
Artemisia	2	1	1	0	3	1
Ambrosia	12	6	2	1	1	1
Cheno/Ams	3	1	2	0	0	0
Salsola	0	0	0	0	0	0
Cyperaceae	4	3	4	1	3	3
Equisetum	1	1	2	0	1	1

St. Louis River Core #2

Number of samples 7

Number of taxa 35

Depth	44	46	48	52	56	60	64
Sample #	44-46	46-48	48-52	52-56	56-60	60-64	64-68
Pinus dip.	3	2	2	5	4	3	4
Pinus hap	4	10	8	8	10	13	11
Pinus undiff	15	12	11	9	11	16	18
Total Pinus	23	23	21	22	25	32	33
Picea glauca	1	0	0	1	0	0	0
P. mariana	0	0	3	0	1	1	1
Picea indet.	2	1	1	0	1	1	2
Abies	1	1	1	1	1	2	1
Larix	1	1	1	0	1	1	1
Cupressaceae	1	2	1	1	2	2	3
Quercus	2	2	1	2	1	4	1
Carya	0	0	0	0	0	0	0
Betula	10	8	9	12	17	15	16
Fraxinus nigra t.	1	0	1	1	0	2	1
Alnus rugosa	3	4	4	4	5	3	5
A. saccharum t.	0	0	0	0	0	1	0
Salix	1	1	2	2	0	1	0
Populus	1	1	0	1	1	1	0
Poaceae	33	37	42	38	35	28	30
Artemisia	1	2	1	1	0	1	1
Ambrosia	5	3	3	3	2	1	0
Tubuliflorae	1	0	1	0	1	1	1
Cheno/Ams	2	1	0	0	0	0	0
Salsola	1	0	0	0	0	0	0
Cyperaceae	5	5	5	5	1	1	0
Rosaceae	1	1	0	0	0	0	0
Equisetum	3	2	2	1	2	1	0
Sphagnum	1	1	0	0	0	0	0
Nuphar	0	0	0	0	0	0	0
Potamogeton	1	1	1	0	0	0	0
Typha	0	1	0	0	0	0	0
Sagittaria	0	1	1	0	0	1	0
Sparganium	0	1	0	1	0	1	1
Degraded	1	2	0	0	0	0	0

St. Louis River Core #3

Number of samples 6

Number of taxa 31

Depth	52	56	60	64	68	72
Sample #	52-56	56-60	60-64	64-68	68-72	72-76
Pinus undiff	18	19	22	18	17	15
Pinus dip.	7	5	6	6	6	7
Pinus hap	7	9	11	10	7	10
Total Pinus	32	33	39	34	30	32
Picea glauca	2	3	1	2	4	4
P. mariana	0	1	1	1	1	0
Picea indet.	0	1	0	1	1	0
Abies	2	1	2	1	1	3
Larix	1	0	1	0	1	1
Cupressaceae	1	2	3	5	2	2
Quercus	2	2	2	3	2	3
Betula	9	11	13	19	16	14
Ostrya/Carpinus	0	0	0	0	1	1
Ulmus	1	2	1	1	1	0
Fraxinus nigra t.	1	1	1	1	1	1
Alnus rugosa	2	4	4	3	6	5
A. saccharum t.	1	1	0	0	0	0
Salix	1	2	0	1	1	1
Populus	1	0	0	1	2	0
Poaceae	25	24	22	20	23	22
Artemisia	1	1	1	1	2	1
Ambrosia	3	6	2	1	1	1
Tubuliflorae	0	1	1	0	1	0
Cheno/Ams	1	1	0	1	1	0
Cyperaceae	5	3	2	2	1	3
Pteridium	1	1	1	0	1	0
Dryopteris	1	0	1	0	0	0
Equisetum	1	1	0	0	1	1
Potamogeton	0	1	0	0	0	1
Typha	1	0	0	0	0	0
Sagittaria	0	1	0	0	1	0

APPENDIX G

QA/QC Data

CHECK STANDARDS

Sample	Name	Sequence	surr. rec	T-Nona (pg/g) after MDL	C-Nona (pg/g) after MDL	T-Chlor (pg/g) after MDL	C-Chlor (pg/g) after MDL	Tox Conc (ng/g) after MDL	% 6 Cl	% 7 Cl	% 8 Cl	% 9 Cl	% 10 Cl	%rec tox	%rec 13C-t-chlor	%rec t-nona	% rec c-nona	% rec t-chlor	% rec c-chlor
sl0060mm	Chkstd 10.25	sl032701	1.013	42.14	23.36	18.94	18.00	10.94	3.2%	24.0%	51.3%	21.0%	0.5%	107%	101%	109%	114%	102%	104%
sl0054mm	Chkstd 10.25	sl032701	0.934	40.59	21.85	19.96	17.49	11.36	2.5%	23.6%	56.4%	16.9%	0.7%	111%	93%	105%	107%	108%	101%
SL0081MM	Chkstd 1.23	sl040201	0.864	4.40	2.09	2.46	2.69	1.04	5.5%	42.0%	35.7%	16.9%	0.0%	104%	96%	103%	109%	101%	105%
SL0073MM	Chkstd 10.25	sl040201	0.958	39.55	22.24	18.77	18.23	10.67	1.1%	20.6%	57.4%	20.0%	0.9%	85%	86%	95%	85%	111%	129%
SL0100MM	Chkstd 1.23	sl041001	0.936	4.85	2.17	2.55	2.63	1.79	1.6%	19.3%	58.7%	20.3%	0.0%	106%	98%	99%	97%	103%	99%
SL0093MM	Chkstd 10.25	sl041001	0.980	38.18	19.91	19.02	17.25	10.85	1.7%	25.2%	48.4%	23.8%	0.9%	145%	94%	105%	88%	115%	126%
SL0138MM	Chkstd 10.25	sl051601	1.062	41.08	21.97	20.17	19.25	6.04	3.2%	34.5%	42.2%	19.7%	0.4%	124%	102%	102%	104%	110%	105%
SL0131MM	Chkstd 4.1	sl051601	1.018	15.69	8.50	8.13	7.27	5.09	5.5%	33.4%	45.0%	16.0%	0.1%	59%	106%	107%	107%	109%	111%
sl0166mm	ChkStd 1.23	sl053001	0.843	4.12	2.45	2.28	1.91	1.64	24.2%	55.3%	18.0%	2.5%	0.0%	133%	84%	89%	100%	103%	92%
sl0171mm	ChkStd 4.1	sl053001	0.938	15.74	8.79	7.26	7.58	5.46	17.6%	43.6%	34.6%	4.1%	0.0%	133%	94%	102%	107%	98%	109%
													MEAN	111%	95%	102%	102%	106%	108%
													STD DEV	25%	7%	6%	9%	5%	12%

BLANKS

sl0049mm	PB003	sl032701	0.664	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0059mm	PB005	sl032701	0.764	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0072mm	PB006	sl040201	0.745	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0079mm	PB007	sl040201	0.658	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0092mm	PB008	sl041001	0.678	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0099mm	PB009	sl041001	0.767	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
SL0130MM	PB010	sl051601	0.908	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
SL0137MM	PB011	sl051601	0.714	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0167mm	PB012	sl053001	0.766	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%
sl0170mm	PB013	sl053001	0.240	0.0	0.0	0.0	0.0	0.0	0.0%	0.0%	0.0%	0.0%	0.0%

Relative Percent Differences (RPD) of Duplicate Analyses

Sample	Name	Sequence	surr. rec	T-Nona (pg/g) after MDL	Surr Corr T-nona	% RPD	C-Nona (pg/g) after MDL	Surr Corr C-nona	% RPD	T-Chlor (pg/g) after MDL	Surr Corr T-chlordane	% RPD	C-Chlor (pg/g) after MDL	Surr Corr C-chlordane	% RPD	Tox Conc (ng/g) after MDL
sl0050mm	419-784	sl032701	74%	0	0.00	0%	0	0.00	0%	165.4478	223.93	200.0%	0	0.00	0%	0
sl0067mm	825-825	sl040201	64%	0	0.00		0	0.00		0	0.00		0	0.00		0
sl0056mm	782-979	sl032701	120%	104.75	87.45	13%	70.26	58.65	1.0%	264.51	220.82	5.6%	131.38	109.68	39%	0
sl0068mm	866-324	sl040201	57%	43.89	77.09		33.05	58.06		118.86	208.78		93.11	163.54		0
sl0088mm	237-660	sl041001	53%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0
sl0161mm	784-920	sl053001	65%	0	0.00		0	0.00		0	0.00		0	0.00		0
SL0125MM	512-455	sl051601	81%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0
SL0126MM	514-050	sl051601	74%	0	0.00		0	0.00		0	0.00		0	0.00		0
sl0097mm	439-525	sl041001	64%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0
sl0168mm	439-525-b	sl053001	74%	0	0.00		0	0.00		0	0.00		0	0.00		0
sl0098mm	504-692	sl041001	69%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0	0.00	0%	0
sl0169mm	504-692-b	sl053001	63%	0	0.00		0	0.00		0	0.00		0	0.00		0