July 1, 1993

LCMR Final Status Report - Detailed for Peer Review-Research

I. Lake Superior Initiative/Institute for Research - Water 19

Program Manager

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A. M.L.91 Ch Sec Subd 4(1) Appropriation $400,000
Balance $0

Lake Superior Initiative-Institute for Research:
This appropriation is to the University of Minnesota Graduate School to establish an Institute for Lake Superior Research that would develop a strong, multifaceted research effort.

B. N/A

C. N/A

II. Narrative

A. Statement of the Problem: Lake Superior requires diligent stewardship to protect its pristine nature during future development and pressures of global change. An effective basic and applied research program needs to be developed to provide a solid basis for policy decisions.

B. Importance: Lake Superior contains 10% of the earth's surface water reserves and is a major economic and recreational asset for the region.

C. Extent of the Problem: No coordinated program of research on Lake Superior currently exists.

III. Objectives

A. To form and staff the Institute for Lake Superior Research.

A.1. Narrative: Criteria for the selection of the director and program heads will be established. A search will be initiated, the permanent director identified and the directors personal lake research program established.

A.2. Procedures: An advisory board representing the Duluth and Twin Cities campuses will be established to set and maintain the direction for the institute. The institute will be in Duluth and for logistical functions would report through the Vice Chancellor for Academic Administration at UMD. The Director will be hired through standard University of Minnesota affirmative action search procedures

A.3. Budget LCMR Funds

a. Amount budgeted: $230,000

b. BALANCE $0

A.4. Timeline for tasks July 91 Jan 92 June 92 Jan 93 July 93

Establish criteria for Director and staff _____
Search for director and staff _____
Program initiation _____

A.5. Status: an advisory board representing both the UMD and Twin Cities campuses was created and criteria developed for the permanent director and staff. An interim Director (Robert Carlson) and interim Associate Director (Robert Holt) began September 1991. Programs were initiated and an equipment infrastructure developed. The search for permanent director and other staff is proceeding to obtain the services of a permanent director by 7/93.

A.6. Benefits: A well-conceived institute will serve to understand and protect its client, Lake Superior. A well defined ILSR will embody superb scientific leadership as well as cost efficiency. The director and program heads will leverage state monies to obtain research funds from federal sources including the National Science Foundation, EPA, and NOAA. These science leaders will lead all phases of planning, proposal preparation, research execution, and publication. The director and program heads will be tenured or on a tenure track within an academic department in the University of Minnesota system.

B. To develop a coordinated program of research on Lake Superior

B.1. Narrative: The presence of three states and a province of Canada on the shores of Lake Superior, necessitates the development of a coordinated research program by all those governmental entities that chose to participate. This need is further emphasized by the commitment of the University of Minnesota to move towards a more integrated program of water related research.

B.2. Procedures: The detailed research plan will be developed from a workshop to be held in Duluth where staff from ILSR and collaborating universities and agencies will gather. This report will be made available to the LCMR and to all participants. In the absence of a permanent Director, funds will be transferred to the program development component to provide a detailed outline of the current knowledge base, the pertinent policy issues and the appropriate research options. This will be developed from 1) the conference to be held in Duluth where staff from the ILSR and collaborating universities and agencies will gather, 2) the previously developed "Needs Assessment" and 3) information synthesized from existing or readily accessible data.

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B.4. Timeline

	July 91	Jan 92	June 92	Jan 93	July 93
Development of a preliminary research program for the ILSR			———	———	
Conduct workshop on the coordination of research on Lake Superior			———		
Develop report on coordinated research program				———	

B.5. Status: Several meetings of the scientific and policy research groups from Michigan Tech., University of Wisconsin, Lakehead University, and the University of Minnesota have resulted in the development of a more coordinated research effort. Moreover, the current status of our knowledge of Lake Superior was the subject of a conference held on November 8-10, 1992 (e.g. "International Symposium on Understanding Lake Superior through Research: Status and Prospects"). The conference attracted about 115 people, including three from Russia, three from Finland and twenty people from Canada. In addition, a cooperative international effort involving Lake Superior with the Russian "Great Lakes" (i.e. Baikal, Ladoga and Onega) has also emerged as a distinctive component of the overall initiative. A set of proceedings are at the collection and editorial stage.

The research program of the Institute began by developing an information base using expertise already at the University of Minnesota. The components of this aspect of the program include:

- The cataloging and preliminary analyses (pollen, nonsiliceous and diatom algae, phytoliths, and mercury) of valuable Lake Superior cores previously collected by Tom Johnson were undertaken. Preliminary analysis indicates that the cores can be dated based on pollen assemblages from Lake Superior. The Bryophyte detritus layer was found at 343.5 cm from a 566 cm long core of the Keweenaw Peninsula represents one of the few datable organic layers in Lake Superior sediments. Historic baseline data for Lake Superior sediments will be obtained from mercury analysis. One publication on the cores has been accepted and three are in preparation. (Huber, Rapp, Glass)

  Under the direction of Professor Thomas Johnson, Geology Department, University of Minnesota, Duluth (UMD), 135 cores were taken throughout the Lake Superior basin. Although Johnson and his colleagues completed specific studies, he left for Duke University in 1983 before most of the cores were systematically logged with general lithologic descriptions. Two cores were analyzed further (S80-1P and VIK83-1G). Analyses included: preliminary pollen, phytolith/diatom, loss-on-ignition, and sediment. Mercury analyses are also underway to contribute baseline data for mercury pollution studies. All of the 135 Lake Superior cores in the possession of the Archaeometry Laboratory, UMD have now been logged, resealed and relabeled for archival and preservation proposes. During the systematic logging a Bryophyte detritus layer was found in core LRTN81-23P at a depth of 343.5 cm downcore.

Six samples from two cores in the western arm of Lake Superior were analyzed for phytolith content. Silica content appears to correlate with depth in the core, not with core location. Three of the samples (Viking 83 core 1G at 25 and 75 cm., SMNS 80 core 1P at 80 cm.) contain well-preserved phytoliths of both grass and non-grass types, as well as diatoms and algal spheres. Three samples from greater depths (SMNS 80 core 1P at 340, 420, and 620 cm.) lack all types of silica microfossils. This distribution could be a result of original deposition patterns, post-depositional degradation, or a combination of both. More detailed examination of the core samples, including comparison to phytolith reference collections from local plant material, can provide additional paleoenvironmental data.

The lower portion of SMNS80-1P core from Lake Superior contains excellently preserved pollen. Pollen found above the 400 cm level is more abundant but not as well preserved. Preliminary analysis indicates that the pollen record from the lowermost samples is late glacial in age.

Detailed pollen analysis has been completed on six samples from 400-635 cm have been analyzed for pollen. From 636-550 cm pollen concentration is low (400-3,000 grains/gram (dry weight)). Pollen concentration increases to 16,300 at 500 cm and declines to 8,900 at 400 cm. The pollen assemblage is dominated by *Pinus* (pine) and *Picea* (spruce). *Picea* declines from 29% at the base to 7.7 % at the top while *Pinus* (mostly diploxylon) ranges from 26% to 55%. Maxima of *Betula* (birch) and *Ulmus* (elm) occur at 550 cm and 450 cm respectively. *Quercus* (oak), and *Fraxinus* (ash) are present at less than 10%. Nonarboreal pollen (NAP) values are low. The most abundant NAP taxa are Cyperaceae (sedge), Gramineae (grass), *Ambrosia*-type (ragweed), and *Artemisia* (wormwood).

Four additional Lake Superior samples were processed using a modification of the method described by Cronberg (1986) for blue-green and green algae analysis. Algae extraction by this method was undertaken to determine if additional phycological information could be attained from the cores. One sample (44-45 cm) from the VIK83-1G core and three samples from the SMNS80-1P core (59-69, 319-320, and 619-620 cm) were processed. Quick scans of these samples indicate that algae abundance is extremely low. However, the samples have a very high clay content which makes analysis very difficult.

In addition to the phytolith samples, diatom extraction was also undertaken on three additional samples: VIK83-1G (74-75 cm) and SMNS80-1P (154-155 cm and 459-460 cm). Quick scans of the phytolith and diatom mounts (Vik83-1G, 24-25 cm; Vik83-1G, 74-75 cm; and SMNS80-1P, 79-80) indicated silica algae spheres, sponge spicules, and several taxa of diatoms. No diatoms, sponge spicules or algae spheres were observed in SMNS80-1P samples 154-155 cm, 339-340 cm, 419-420 cm, 459-460 cm, or 619-620 cm.

In order to obtain a more complete understanding of the depositional record, loss-on-ignition of organic and carbonate carbon was undertaken on the Lake Superior cores. Carbonate and organic carbon content provide an independent means of interpreting the stratigraphic sequence which in turn can be correlated with the pollen assemblages. Changes in the carbonate and organic carbon content of sediment may also indicate environmental changes occurring in the watershed and the catchment basin through time. This information can be used to reconstruct past paleoenvironmental conditions.

Organic carbon content in both cores are low, 7% or less. Organic carbon varies from 5.2% to 6.2% in the VIK83-1G core and from 3.3% to 7.0% in the SMNS80-1P core. Carbonate carbon is very low in the VIK83-1G core, ranging from 2.7-3.7%. In the SMNS80-1P core, carbonate content is variable and attains a maximum value of 13.3%. The higher carbonate carbon values in different sections of the core were also observed during hydrochloric acid tests while undertaking lithologic descriptions.

Based on this preliminary palynomorph investigation, manuscript Contribution 93-1 from the University of Minnesota, Institute for Lake Superior Research has been accepted for publication by *Current Research in the Pleistocene*, volume 10.

- A new technique was developed to analyze toxic contaminants in extracts of sediment samples. The technique involves the introduction of a constant source of volatile organic surrogate for known biological targets into a mass-spectrometer. Concurrently, the effluent stream from a gas chromatograph passes through the same mass spectrometer and the components that display biological interest are interrupted by the surrogate and exhibit characteristic behavior in the analysis chamber of the instrument. This remarkable ion-molecule reaction protocol scheme may revolutionize analysis of complex mixtures and has been the basis for a well-received presentation at a national meeting and a manuscript currently in preparation (Rosynov and Carlson)

  An evaluation of the structural characteristics of the various classes of toxic compounds indicate that the vast majority have functionality with inherent electron insufficiency (i.e. electrophilic character). Additional support for the importance of electrophilic reactivity to biological processes can be derived from the observation that the nucleophilic addition of the sulfur of cysteine or glutathione to members of several classes of these compounds results in the loss of biological activity.

  Epoxides, as a class of reactive and carcinogenic electrophiles, have generated much interest because of their formation during metabolism or photo-chemical oxidation of aromatic compounds and because of their production in large quantities as industrial intermediates. These electron-deficient species are known to form covalent adducts (i.e. "conjugate") with the manifold electron-rich (i.e. nucleophilic) sites in DNA or proteins. Moreover, a constant ratio has been observed for DNA / protein adduct formation over a wide concentration range for several reactive environmental toxicants.

  The ability to generate and detect products of model protein (i.e. HS-groups) or DNA interactions with electrophilic mutagens was demonstrated by ion-molecule reactions in the collision cell of a triple quadrapole tandem mass spectrometer. Reactions were observed between mass-selected epoxides eluting through a leak valve into the collision cell. The daughter- and parent-ion mass spectra of the reaction were obtained and confirm the ability to detect substitution products (i.e. "conjugation") formed in the collision cell. This illustrates the potential for the development of rapid and sensitive methods for screening complex environmental matrices for carcinogenic epoxides, as well as for evaluating the mutagenic potential of related contaminants possessing electrophilic character.

- A set of investigations on Lake Superior was initiated that used conceptual and mathematical models that have already been successfully applied to a geochemically related large freshwater lake in Russia (Lake Ladoga). These studies have examined organic matter degradation, nutrient and trace metal cycling, temperature effects over the near and long term and sediment oxygen diffusion and consumption. A minimum of 3 publications will result from this effort over the next 2-3 months. (Melnichuk and Carlson)

  The objectives of the research during March-June 1993 were as follows: 1) To modify models of organic matter degradation, nutrient and trace metal cycling to incorporate Lake Superior. 2) To compare the biogeochemistry of Lake Superior and Lake Ladoga (Russia). 3) To advance a long term time scale conceptual model of Lake Superior carbon cycling. 4) To continue a discussion on the theoretical aspects of early diagenesis (i.e. in Geochem. Cosmochim.)

  It was found that the most suitable place for the application of the model of organic matter (OM) degradation and oxygen consumption was the area surrounding the WLSSD outfall into the St. Louis River. It is proposed to use additional water circulation and aeration as a method for improvement of sediment and water column quality in this area.

  The probability of secondary contamination in Lake Superior by Cu, Pb, Cd, etc. was deduced from: 1) Their high mobility at the sediment-water interface in Lake Superior, 2) The similarity in the biogeochemical processes in Lake Superior and Lake Ladoga, 3) Secondary pollution of Lake Ladoga bottom water. In particular, the dissolved carbon (DOC) trends in Lake Ladoga, which may be compared with North American Great Lakes is presented. It also is suggested that models of OM degradation and sulfate reduction will be useful for the long-term prediction of sediment quality with respect to toxic metals.

  A conceptual model of Lake Superior carbon cycling on a 10 - 10,000 year time scale was proposed to study effects of global warming and for the reconstruction of past climatic changes. The model is based on an empirical relationship (Johnson et. al., 1982) between organic carbon (OC) flux in sediments with primary production, OC sediment degradation (Emerson et. al., 1985) and a sediment oxygen diffusion and consumption (Brostrom & Melnichuk, in prep.). By using this approach, the assessment of variability of the sedimentary remineralization rate constants for laminated and bioturbated Lake Superior sediments was performed. It was proposed to use the rate constant values for OC degradation to determine Lake Superior global carbon cycling.

  A list of selected critical issues of early diagenesis theory was proposed to revise several basic assumptions for mathematical modeling of nutrient and toxic metal cycling in large lakes and in other freshwater bodies.

- Steady progress has been made on the development of a high resolution basin analysis of Lake Superior and the effects of lake levels on sedimentation patterns. Specific aspects of the program included: 1) The beginning of an intensive data rescue of previous basin analysis and quaternary research on Lake Superior, 2) The use of prior high-resolution seismic profiling to show evidence of significant variation since the Ice Age, 3) The development of a seismic profiling and data reduction infrastructure, 4) The synthesis of available data in the form of sediment maps and profiles. A monograph which documents the broad range of bottom reflection characteristics from Lake Superior should be completed by the end of summer, 1993 (Kelts and Graber).

Several thousand kilometers worth of original seismic profiles were obtained from Prof. Tom Johnson. In addition, negatives of thousands of km of sparker records taken in 1966 were borrowed from Dr. Richard Wold. These negatives have been digitized and the originals will be returned to Dr. Wold at the end of June. Core data records and core photographs from all the major coring done in the last 30 years have been received from Dr. William Farrand, The National Water Research Institute, located in Burlington, Ontario, and from Prof. Tom Johnson. These are now being archived.

An extensive bibliography of past and present research work done on the Lake, along with names and addresses of people and organizations who are doing current research or are interested in collaborating on projects pertaining to the Lake has been compiled. Maps for Lake Superior, including sediment distribution, and bedrock topography have been obtained. There are 5-10 year plans to complete a digitized bathymetric map, which is necessary for interpreting seismic data. The Canadian Hydrographic Service has seven quad. sheets digitized for Lake Superior and is sending this data. NOAA has also done extensive bathymetric digital soundings across the lake. The dot- maps of these soundings are being obtained. NOAA is very interested in collaborating on this compilation and other projects regarding the Lake.

Much effort has been spent analyzing the high-resolution seismic profiles from Tom Johnson. The ship tracks of all the cruises, and the digitized seismic cross sections have been mapped and correlated with the cores and bathymetric cross sections. We have targeted special areas in Lake Superior where further high-resolution profiles are needed in order to see lake level changes. Compiling a seismic stratigraphy has proved to be difficult because ground truth data on which to base stratigraphic assumptions is lacking.

The objectives of this pilot project are well on the way to completion. Many people have graciously contributed information and data to this project. As a result, the U of MN is on its way to becoming the archive center for quaternary data on Lake Superior. Initial analyses of the seismic profiles from Tom Johnson has given us considerable information on the lake basin floor showing much greater diversity than expected. Improved resolution will now be possible with the acquisition of the new GEOPULSE sub bottom profiling system . Longer cores will be needed in order to calibrate a seismic stratigraphy and to determine the timing of significant lake level changes. Initial testing of the new seismic system are expected in August 1993.

- <u>The investigation of the accumulation and sources of natural and anthropogenic organic chemicals in Lake Superior Sediments.</u> The objectives of this research were to determine the sources, both natural and anthropogenic, transport and accumulation rate of sedimentary organic matter in Lake Superior. Three dated cores sampled in the western basin of the lake were analyzed. The sediments were extracted with CH_2Cl_2 and the organic extract was fractionated in a chromatographic column (Si/Al) in three fractions. The first fraction contains aliphatic compounds, such as fatty acids and fatty alkanols. All fractions were analyzed in gas chromatography coupled with mass spectrometry (GC/MS).

  Sediment accumulation rates for the three cores, obtained using ^{210}Pb geochronology, increased after World War II but have decreased since the early 1970's in the Duluth basin, whereas they have remained constant in the open lake.

n-Alkanes dominated the aliphatic fraction in the Lake Superior cores. These compounds have natural and/or anthropogenic sources. Their distribution patterns show that autochthonous organic matter (represented by the lower molecular weight n-alkanes) is not well preserved in the oxic sediments of the lake and consequently recycled in the water column. Also autochthonous productivity although low (oligotrophic system) is higher toward the Duluth site possibly due to additional nutrient inputs from the land. Allochthonous natural organic matter from terrestrial higher plants (represented by the higher molecular weight n-alkanes) is better preserved in the sediments. In contrast to the autochthonous organic matter, no important difference in the accumulation rate of the allochthonous organic matter is observed between stations as the distance from their coast is similar. Atmospheric transport (pollen) seems the main mode of transport of these compounds.

n-Alkane accumulation rates in the sediments ranged from 100 ng/cm^2/yr in the open lake to 400 ng/cm^2/yr in the nearest Duluth station. Atmospheric deposition of n-alkanes in Lake Superior is about 40 to 100 ng/cm^2/yr. This strongly suggests that atmospheric deposition is the major mode of transport of terrestrial organic matter in the open lake.

An Unresolved Complex Mixture (UCM_{23-35}) in the aliphatic fraction chromatograms reflects contamination from degraded petroleum. Petroleum inputs began by 1900 and became more important toward the west end of Duluth basin, and decreasing towards the open lake where there was no indication of petroleum contamination. These results indicate that the western site of the Duluth basin is a source of this input. Petroleum inputs were higher prior to 1965 (maximum 1950-65) than today.

Polycyclic Aromatic Hydrocarbons (PAHs) originate mainly from combustion of fossil fuels. Their accumulation rates ranged today from 10 ng/cm^2/yr in the open lake to 25 ng/cm^2/yr in the west part of Duluth basin. The higher accumulation rate (3x the actual values) was observed in Duluth basin in 1965 (60 ng/cm^2/yr). PAH results were in agreement with previous investigations in the lake (e.g., Gschwend and Hites, 1981; McVeety and Hites, 1988; Baker, Eisenreich and Eadie, 1991). Long range atmospheric transport is the main source of PAHs in the open lake whereas other sources (discharges from urban areas and short range atmospheric transport) contribute in the Duluth basin. Specific PAH ratios, as sources indicators, show that residential wood and oil combustion, automobile exhaust and coal burning contribute to the PAH loading in the area.

A comparative investigation with Lake Victoria sediments was also performed as a potential indicator of ecosystem change.

- In summary, the development of the information base has been significant in scientific quality and will be an integral part of subsequent decisions on research direction that will be made by the new Director. However, if the delays in the Director search would have been realized earlier in the process, the implementation of these activities would have been initiated several months sooner.

B.6. Benefits: Increased cost efficiency and productivity will develop by operating from a coordinated research agenda and from having an improved information base.

IV. Evaluation: For 1991-92 the program can be evaluated on the quality of the director that is hired and of the preliminary research plans that are developed. In 1992-93 research results will be available as well as a report outlining a coordinated research program for Lake Superior.

V. Context:

A-C. Phase I of the Lake Superior Initiative was funded by the Graduate School (U of MN), the U of MN-Duluth, NRRI, and the MN Sea Grant College. Activities resulted in a well-defined agenda for research in the physical, chemical, and biological sciences directed to a detailed understanding of the Lake Superior ecosystem. Cost: $27K.

Phase II, conducted by the staff of SRI International, recommended the administrative structure and relationships for the institute. It was funded by LCMR for $50K, and has resulted in a core/network model for scientific leadership, administration, and outreach.

Phase III, per this request, will begin to staff the institute and provide for planning.

D N/A

E. The Biennial Budget System Program Title and Budget is not available at this time.

VI. Qualifications:

1. Program Manager

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1991 RESEARCH PROJECT ABSRACT
FOR THE PERIOD ENDING JUNE 30, 1993
This project was supported by the MN Future Resources Fund

TITLE:	Lake Superior Initiative/Institute For Research
PROGRAM MANAGER:	Dr. Robert M. Carlson
ORGANIZATION:	University of Minnesota
LEGAL CITATION:	M.L. 91, Ch. 254, Art. 1, Sec. 14, Subd. 4(1)

STATEMENT OF OBJECTIVES

The University of Minnesota was to form and staff the Institute for Lake Superior Research and to develop a coordinated program of research on Lake Superior.

RESULTS

The University appointed an Interim Director (Dr. Robert Carlson) and Associate Director (Dr. Robert Holt) and has moved forward to obtain the services of a permanent director by July 1993.

The research program of the Institute began by bringing together science and policy research groups from Michigan Technological University, University of Wisconsin, Lakehead University and the University of Minnesota in a conference to ascertain the current state of knowledge of Lake Superior (November 8 - 10, 1992; "International Symposium on Understanding Lake Superior through Research: Status and Prospects"). The Conference attracted 115 people including three from Russia, three from Finland and twenty people from Canada. In addition, an information base was developed using expertise already available at the University of Minnesota. This included:

- The cataloging and partial analysis of previously unexamined Lake Superior core samples for pollen and mercury content.

- The discovery of a new method for the analysis of reactive toxicants in complex matrices such as sediments using a constant supply of a surrogate for known biological targets to interact with the effluent from a gas chromatograph inside a mass spectrometer.

- A set of investigations on Lake Superior (e.g. organic matter decomposition, nutrient and trace metal cycling and temperature effects) using conceptual and mathematical models that had previously been successfully applied to a geochemically similar large freshwater lake in Russia (Lake Ladoga).

- A study by the Limnological Research Center on the high resolution basin analysis of Lake Superior and the effects of lake levels on sedimentation patterns.

- An investigation of the accumulation and sources of natural and anthropogenic organic chemicals in Lake Superior sediments.

PROJECT RESULTS: USE AND DISSEMINATION

The major mechanism for the dissemination of results will be the publication in referred journals in the specific area of study. Currently, a minimum of 8 such publications are in preparation or have been accepted. A proceedings from the Lake Superior Research Conference (November, 1992) will be published and made available in 1993.