Date of Report: December 31, 1997

LCMR Final Work Program Update Report

I. Project Title and Project Number: I-11 /I-15 Mercury Deposition and Lake Quality Trends

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A. Legal Citation: ML 95 Chp. 220, Sect. 19, Subd. 5(g).
and ML 96 Chp. 407, Sec. 8, subd. 9.

Total Biennial LCMR Budget: $250,000.

Balance: $ 3,000

Appropriation Language: $120,000 of this appropriation is from the future resources fund and $130,000 is from the Great Lakes protection account to the commissioner of the pollution control agency for an agreement with the University of Minnesota-Duluth to synthesize and interpret a five-year (1990-1994) mercury deposition data base and evaluate water quality and fish contamination trends for 80 high-value lakes and compare it with historic data. This is to be done in cooperation with the pollution control agency. Data compatibility requirements in subdivision 15 apply to this appropriation.

The availability of the appropriations for the following projects is extended to December 31, 1997, when projects must be completed and final products delivered: Laws 1995 chapter 220, section 19, subdivision 5 paragraph (g), mercury deposition and lake quality trends; ...

B. LMIC Compatible Data Language: Not applicable.

C. Status of Match Requirement: none required

II. Project Summary:

This project is designed to establish current ecological health conditions and evaluate trends for lake watersheds, water quality, toxic contamination, bioaccumulation and effects on fish, and mercury and acidic deposition from precipitation in Minnesota.

Water quality and toxic contamination levels in game fish for each of 80 high-value lakes will be measured to ascertain current conditions in those lakes. These measurements will then be compared with historical data for those lakes to assess trends in fish contamination (80 lakes) and water quality (approximately 70 lakes) and will also be useful for making any future comparisons. The rates of change for contaminant levels in fish, effects on fish health, and water quality parameters and the significance of the change will be analyzed and assessed. Analyses results on toxic residues in game fish will be presented for mercury and, on a selected sample basis, other heavy metals and chloro-organics. Acid neutralizing capacity (ANC), pH, turbidity, color, and electrical conductivity will be presented from the analyses of water samples for each lake watershed using identical techniques and equipment to facilitate high accuracy comparisons. Watershed characteristics, factors, and loadings correlated with water quality, toxic residues in fish, and ecological health measures will be used to identify causal mechanisms.

Results will be interpreted from a 5-yr, 1990-1994, mercury wet deposition monitoring network in terms of regional meteorological patterns, seasonal and yearly trends, relationships with acidic deposition and other ions, and comparisons with emission source areas, inventories, and deposition standards. Because the primary source of mercury to

Minnesota lakes is through atmospheric deposition, these data and interpretations will be useful in conjunction with the environmental protection and assessments of water quality and identifying causal mechanisms leading to toxic levels in fish and ecological health impacts.

III. Work Program Update Summary:

MERCURY DEPOSITION TRENDS SUMMARY:

Mercury Wet Deposition Study. From 1990 through 1996 precipitation data were collected for total mercury wet deposition at 11 sites located in Minnesota, North Dakota, and Michigan . Six of those sites have 6 years of continuous weekly sampling data which are the main focus of this report. Also summarized are the results of methylmercury measurements conducted in 1993 from 7 sites. A draft manuscript summarizing the results (1990-1995) is being revised and will soon be submitted for journal peer review. See attached report for figures summarizing those results. Among the findings were the following:

Precipitation monitoring was conducted weekly for six years at six sites (Bethel, MN; Cavalier, ND; Duluth, MN; Ely, MN; Int'l. Falls, MN; Lamberton, MN) located throughout Minnesota. The measurements included rain and snow fall volumes, and total and methyl mercury. Monitoring sites were named for the closest town or city. Other sites (Finland, MN; Marcell, MN; Minneapolis, MN; Raco, MI; Tower, MN) were also monitored for shorter durations.

The total mercury deposition (micrograms per square meter) annual mean value was found to be 6.7 ±1.8 (S.D.), 6.9 ±1.4, 4.6 ±1.0, 7.3± 1.5, 8.6± 0.6, and 9.0± 2.5, respectively, for the years 1990-1996. Regression analysis for combined individual site annual average wet mercury deposition values versus time gives a significantly positive, non-zero slope of 0.55 $\mu g/m^2 yr$. Hg, ± 0.18 (S.E.). Data for each site are plotted and tabulated in the attached report.

Temporal comparisons (annually and quarterly) of mercury deposition, averaged across the six long-term sites, show the bulk of the mercury mass is deposited during the warmer rain season.

A t-test statistical analysis showed the 3 northern most sites (Cavalier, Ely, and International Falls) were significantly lower ($p < 0.003$, 1 tail) in deposition than the other 3 sites (Bethel, Duluth, and Lamberton).

Extensive quality assurance measurements were made to verify precision and accuracy of precipitation sampling and mercury analysis methodology. Total mercury measurements in precipitation were performed by two independent methods of analysis in different laboratories. The results of these inter comparisons show that atomic absorption and fluorescence agree within 96 - 110 % of each other over the range 2 to 30 ng/L in precipitation samples.

Total mercury in precipitation is composed of approximately 2% methylmercury, the most toxic form. The methylmercury wet deposition correlates strongly with total mercury (+0.75), nitrate (+0.72), and sulfate (+0.78).

Preliminary statistical analyses comparing mercury deposition and total coal consumption (Minnesota and border states) showed a relatively consistent annual pattern and a strong positive correlation.

LAKE QUALITY TRENDS SUMMARY

A Bench-Mark Concept Fish Database. A successful fish sampling program was completed for eighty Minnesota lakes by Department of Natural Resources regional staff personnel over the two year period, 1995-96. Eight to ten specimens from each lake were obtained and measured over a range of desired sizes. On this extensive collection of samples, more than 1,400 mercury analyses were performed to completely characterize the specimens and generate the necessary database needed to make quantative comparisons with data obtained previously from the same lakes 3 to 20 years earlier. This extensive database is also useful in identifying the watershed factors which may be responsible for different degrees of fish condition as well as to determine mercury bioaccumulation mechanisms.

Mercury in Fish Comparisons. Comparisons of past and present data are complicated due to a number of different factors. Most commonly, data for each lake comparison was different in some respect: different numbers of fish, different dates of sampling, and different ways of analyzing the fish tissue. These factors were addressed to the extent possible and the resultant differences may, for the most part, represent actual changes in fish population mercury residue levels. Additional work is underway to understand more completely what these differences represent.

The results of our findings to date indicate that out of 75 study lakes (with sufficient historical data for statistical comparisons) 43 lakes (57%) show lower fish mercury levels for recent data compared to those reported previously, while 19 lakes (25%) show greater mercury concentrations, and 16 lakes (17%) show no significant difference.

Of those lakes having fish with less mercury, the average differences for northern pike are 213 ng Hg/g tissue (a 36% lower difference, on average) and for walleye are 268 ng Hg/g tissue (a 30% lower difference, on average).

For those lakes showing more mercury, the average differences for northern pike are 165 ng Hg/g tissue (a 53% higher difference, on average) and for walleye are 165 ng Hg/g tissue (a 72% higher difference, on average).

Since each lake is different with regard to the various factors influencing the comparisons, separate plots for each lake are provided showing the recent and historical mercury data, along with a more detailed explanation in the attached report.

Mercury Effects on Fish Fecundity. Twelve northern pike spawning pairs (matched by size rank) were collected from 3 study lakes. Mercury concentrations and lengths for those fish ranged from, 172 - 2038 ng/g and 49.6 - 89.0 cm, respectively, for males and 213 - 1257 ng/g and 44.9 - 87.8 cm for females. It was found that mercury concentrations in sperm (average = 114 ng/g, range = 9 - 700 ng/g) were much higher (>10X) than in eggs (average = 10 ng/g, range 1 - 53 ng/g). The eggs were fertilized and incubated at the French River fish hatchery. Although no differences in egg hatch yield or fry behavior were observed, the results may have been confounded by experimental conditions that were dictated by fish hatchery operations.

Water Quality and Related Trends. Preliminary statistical analyses comparing past and present measurements are in progress and results are expected within three months.

IV. Statement of Objectives:

Objective A - Ascertain water quality, toxic contamination, and ecological health conditions for 80 lakes, 70 from the Minnesota Department of Natural Resources (MDNR) Region 2, the region showing the largest degree of fish contamination in high value lakes.

Each of the study lakes will be sampled for game fish, other biota, and water. Fish and other biota will be analyzed for mercury and, on a selected sample basis, other heavy metals and chloro-organics content. Ecological health will be measured by fish growth and condition, primary productivity, in some watersheds, reproduction. Water will be analyzed for ANC, pH, turbidity, color, electrical conductivity, plankton (size >80μ), and trophic status (secchi depth). These data will be organized to facilitate historical and future comparisons. The selection of previous studies (watershed/water quality and fish contamination) and by consideration of lakes selected for MDNR fish surveys. Consultations with the manager of the proposed sediment core study, I-9, will also continue throughout the study lake selection stages of both projects in an effort to maximize the number of lakes of common interest. A goal is to include as many Minnesota lakes as possible with historical data of appropriate quality in order to provide the maximum resolution of any trends.

Objective B - Evaluate water quality, toxic contamination, and bioaccumulation trends, ecological health, and watershed factors which may be casually related.

New water quality, toxic contamination, and ecological health conditions ascertained under Objective A will be compared with historical data generated from 1976 - 1992 to establish and evaluate water quality and fish contamination trends. Watershed factors influencing water quality, ecological health, mercury residues in fish and biota, and rates of change in mercury bioaccumulation will be identified using correlation and regression analyses.

Findings under this objective are designed to elucidate causal mechanisms that are directly applicable to the study watersheds and generally applicable to the immediate region they are from. It is not the intent of this project to characterize all Minnesota watersheds based on the study of 80 lakes. However, some general inferences may be made regarding relationships that are found. For example, if certain watershed factors are found to strongly influence water quality or fish bioaccumulation trends for the 80 lakes, then it is reasonable to expect that these factors could also be important to Minnesota lake watersheds that exhibit the same watershed characteristics.

Objective C - Synthesize, interpret, and report results for a 5-year mercury and major ion deposition data base.

Because mercury contamination in Minnesota lakes is primarily derived from atmospheric deposition, it is important to better understand the characteristics of this phenomena. The goal of this objective is to evaluate and characterize the mercury deposition data collected in the Minnesota region to date.

Mercury concentrations and wet depositions have been monitored at 8 regional sites co-located with federal and/or state acid-rain deposition monitoring stations. Acid, major ion, and mercury depositions will be characterized in terms of regional meteorological patterns, seasonal and yearly trends, emission source areas, and relationships with other deposition ions.

Timeline for Completion of Objectives:

7/95 1/96 6/96 1/97 6/97

Objective A. Ascertain water quality and toxic contamination conditions for 80 lakes.

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Objective B. Evaluate water quality and toxic contamination trends and watershed factors.

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Objective C. Synthesize, interpret, and report results for a 5-year mercury deposition data base.

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V. Objectives/Outcome:

A. Title of Objective/Outcome: Ascertain water quality, toxic contamination and ecological health conditions for 80 study lakes.

A.1. Activity: Fish population health and water quality survey sample collection.

A.1.a. Context within the project: Samples collected from each lake during 1995 and 1996 will provide the basis for defining conditions for those years.

A.1.b. Methods:

Lake selection: Study lakes selection is based on the following considerations:

1) existence of fish populations and adequate historic (fish residue analyses data. A minimum number of three fish data points are needed for a regression analysis of fish mercury concentration vs size for a particular lake, species, and sampling year. This allows some quantification of uncertainties regarding regression results.
2) existence of adequate historic water quality data. Important water quality measurements include pH, ANC, conductivity, color, and total organic carbon. Concentrations of mercury in water, mercury in plankton, and major ions, as well as

lake morphometry data, and watershed characteristics (e.g. land use, forest cover etc.) are also desirable.

3) availability of walleye or northern pike. The reason for choosing these species are discussed below.
4) geographic location and overlap with project I9 - Ten lakes will be selected from around the state in consultation with the project manager of I9 for this purpose.
5) toxic residue levels in fish - Lakes with higher contamination will have more representation.
6) lake water quality - The ensemble of lakes must have diverse water quality and morphometry. A diverse selection strengthens statistical interpretations.

Criteria 1 and 2, above, are the most important because of the trend evaluations of both mercury in fish and water quality obligated under objective B. Criteria 3 is an effort to keep the fish study robust without the confounding issue of mercury bioaccumulation differences across different species. Northern pike and walleye were selected because they are the most commonly sampled of the game fish and their mercury contamination relationships have been previously studied (Sorensen *et al.*, 1990).

Studying game fish is preferred over forage fish for this project because 1) there is more historical data for game fish and 2) game fish are more mobile than forage fish and are, thus, better integrators of bioaccumulation variations across lake zones.

The available set of lakes that have sufficient historical data (100 - 200 lakes) for walleye or northern pike are listed by Helwig and Heiskary (1985) and MDNR (1994). The most comprehensive data available on water quality is available for 267 lakes (Rapp *et al.*, 1985). A comparison of these two sets revealed 70 lakes common to both. Because this project seeks to maximize statistical interpretations of mercury contamination and water quality trends, all 70 lakes are proposed for this study.

Because the 70 proposed lakes are all located in Minnesota Administrative Region 2 (MDNR, 1994), ten additional lakes will be selected to provide a two lake representation from each of the other 5 Minnesota DNR Administrative Regions. All lake selections will be made in cooperation with planners of project I9 and the MDNR annual monitoring program.

The set of 70 proposed lakes selected for review by the MDNR, Minnesota Pollution Control Agency (MPCA), and project I-9 staff are listed in Table 1. Most of these lakes were studied previously for water quality characterization and acid deposition impacts (Rapp *et al.* 1983) and for mercury levels in water, sediment, plankton, and, in most cases, fish (analyzed by the Minnesota Department of Health) (Sorensen et. al. 1990). Up to 20 lakes from this present list will be sampled for fish by MDNR staff during the summer of 1995 and 1996 as part of their planned activities. For sampling the remaining lakes, the MDNR will provide supervision from area offices for project hired field crews. This will ensure the quality of all collected data as well as reduce project costs (see attached letter from Skrypek to Glass, January 27, 1994).

General: The study lakes will be sampled during fish spawning and field surveys (June-August, 1995 and 1996) for fish and during the spring and fall, when the water column is mixed, for water quality. A subset of the 80 lakes will be sampled twice (spring and fall) for all parameters with the intent of assessing seasonal variabilities and for comparisons with previously collected water quality data (Glass *et al.*, 1985). An additional subset of up to 10 lakes will also be sampled during fish spawning to determine egg hatchability as a function of mercury residue levels.

Fish sampling: Fish sampling and measurements will be done under the supervision of staff from the MDNR during the summer field surveys of 1995 and 1996 using gill nets and trap nets and during spring spawning using trap nets. General methods used for this activity are described in more detail in MDNR (1993). Fertilized eggs, from five individual pairs, will be transported to nearby hatcheries for incubation. Fish will be kept on ice or frozen until transported to the University of Minnesota Duluth (UMD) Limnology Laboratory where they will be kept frozen until analyzed.

The goal is to sample up to 10 game fish of diverse size of one or two species from each study lake. The target species (either northern pike or walleye) for each lake will depend on the availability of historical data. If historical data exists for more than one species for a particular lake, then the species which is more in common

Table 1. List of Proposed Study Lakes[a]

Lake Name	County	Surface Area (ha)	Lake No.
Adams	Lake	197.9	38-0153
Alton	Cook	390	16-0622
Ash	St.Louis	278.4	69-0864
August	Lake	76.9	38-0691
Ball Club	Cook	82.4	16-0182
Basswood*	Lake	10669.5	38-0645
BearHead	St. Louis	264.8	69-0254
Bear Island	St.Louis	914.7	69-0115
Big	St.Louis	762.4	69-0190
Big Moose	St.Louis	411.4	69-0316
Birch*	St Louis	2499.5	69-0003
Black Duck	St.Louis	498.9	69-0842
Browns	Lake	85	38-0780
Burntside*	St.Louis	2950.1	69-0118
Clara	Cook	158	16-0365
Crane*	St.Louis	1196.0	69-0616
Devil Track	Cook	743.7	16-0143
Dunnigan	Lake	32.6	38-0664
Echo	St.Louis	454.6	69-0615
Elbow	St.Louis	687.4	69-0744
Fall*	Lake	884.7	38-0811
Fraser	Lake	284	38-0372
Gabimichigami	Cook	483.1	16-0811
Garden	Lake	253.9	38-0738
Ge-Be-On-Equat	St.Louis	267.3	69-0350
Greenstone	Lake	134	38-0718
Gunflint*	Cook	1636.8	16-0356
Horse	Lake	282	38-0792
Hustler	St.Louis	108.5	69-0343
Isabella	Lake	516.2	38-0396
Jeanette	St.Louis	241.0	69-0456
John	Cook	76	16-0035
Johnson	St.Louis	683.8	69-0691
Kabetogama*	St.Louis	10424.9	69-0845
Kjostad	St.Louis	179.3	69-0748
Lac La Croix	St.Louis	12154.4	69-0224
Little Cascade	Cook	107.0	16-0347
Little Saganaga	Cook	669	16-0809
Little Trout	St. Louis	105	69-0682
Little Vermilion	St. Louis	431	69-0608
Loon	Cook	451.6	16-0448
Loon	St.Louis	946.6	69-0470
Moose	St.Louis	373.2	69-0806
Mukooda	St.Louis	313.9	69-0684
Namakan*	St.Louis	5685.9	69-0693
Nels	St. Louis	71	69-0080
Newton	Lake	210	38-0784
Ninemile	Lake	121	38-0033
Northern Light	Cook	134.9	16-0089
Oyster	St.Louis	310.9	69-0330
One	Lake	289	38-0605
Parent	Lake	180.3	38-0526
Pelican*	St.Louis	4663.0	69-0841
Rainy*	St.Louis	89356.6	69-0694
Saganaga	Cook	7373.6	16-0633
Sand Point*	St.Louis	3419.4	69-0617
Sandpit	Lake	23.6	38-0786
Sawbill	Cook	340.3	16-0496

Sea Gull	Cook	1625.5	16-0629
Shagawa	St.Louis	941.4	69-0069
Slim	St.Louis	126.1	69-0181
Snowbank	Lake	1860.4	38-0529
Tom	Cook	165.4	16-0019
Tooth	St.Louis	23.9	69-0756
Triangle	Lake	122	38-0715
Trout*	St.Louis	3309.4	69-0498
Vermilion*	St.Louis	12383.8	69-0378
White Iron*	St.Louis	1277.9	69-0004
Wilson	Lake	260.3	38-0047
Windy	Lake	184.4	38-0068
Possible alternates:			
Frost	Cook	133.6	16-0571
Homer	Cook	177.1	16-0406
Kawishiwi	Lake	158	38-0080
McDonald	Cook	35.1	16-0235

[a]Lake identification number (MCD, 1968)

* Indicates fish contamination data is available from the 1970's.

Table 1 Addendum: List of Proposed Additional Study Lakes from other State Regions[a].

Lake Name	County	Surface Area (ha)	Lake No.
Region 1			
Julia	Beltrami	199	04-0166
Blackduck	Beltrami	1110	04-0069
Region 3			
Stevens	Cass	57	11-0116
Washburn	Cass	715	11-0059
Region 4			
Big Kandiyohi	Kandiyohi	1200 (est.)	34-0086
Hendricks	Lincoln	661	41-0110
Region 5			
Fountain	Freeborn	225	24-0018
Mazaska	Rice	278	66-0039
Region 6			
Wirth	Hennepin	15	27-0037
Harriet	Hennepin	136	27-0016

[a]As defined by MDNR (1994).

[b]Lake identification number (MCD, 1968)

with that chosen for other lakes will be selected. Desired fish size ranges are approximately as follows: northern pike - 30-80 cm and walleye - 20-60 cm.

Water sampling: Water will be sampled by UMD personnel during the fall turnovers of 1995, 1996, and a subset during spring turnovers of 1996 and 1997. All water samples will be transported and stored at 4°C until analyzed. Samples for mercury analyses will be preserved immediately with a nitric acid/potassium dichromate or nitric acid/gold trichloride solution, or other suitable matrix.

Field measurements: Field water quality measurements will be made in conjunction with water sampling and will consist of conductivity and temperature (YSI model 33) profiles (surface, mid-depth, and bottom), and lake water transparency using a Secchi disc.

Other biota: Plankton will be sampled using a Wisconsin style net (Wildco Wildlife Supply Co.) and a Minnesota plankton bucket (J. Shapiro, U. of Minnesota, Mpls, MN) and the methods described in Sorensen *et al.* (1990). lake. Samples will be transported and stored at 4°C until analyzed for mercury content.

Quality Assurance: Water and plankton samples and field measurements will be replicated (two sets of samples and measurements taken) at every 10th site. All samples collected for trace analyses will be handled appropriately to avoid contamination. This includes using gloved hands (new gloves for every sample) and keeping water sample bottles double bagged. All sampling locations will be documented using maps, field sheets and notes, and where necessary, photographs.

Data Management: All field measurements and sample history will be recorded in standard bound notebooks in the field. Each entry will include the date of sampling, the assigned site number, the geographic position of the site, field measurements, and the names of the technicians who performed the sampling. Any sampling problems that may cause sample contamination or affect the sample integrity will also be recorded in the field notebook as well as reported to the project manager upon return from the field. After field work is completed, the logbooks will be archived in a designated area at the Archaeometry/Limnology Laboratory at UMD. Various field notebook entries will be included in the computer data base containing all measurements as deemed appropriate.

A sample number code will be assigned to each sample in the laboratory. The code will indicate water body (using codes listed by MCD, 1968), sample type, date collected, and analysis type (e.g. normal, field replicate, lab duplicate, spike, etc.)

A.1.c. Materials: gill nets, trap nets, polyethylene sample bottles, plankton net, field conductivity and temperature meters, freezers, coolers, motorized boats, camera, and maps.

A.1.d. Budget:

Total Biennial LCMR Budget: $50,000
LCMR Balance: $0

A.1.e. Timeline:	7/95	1/96	6/96	1/97	6/97
product 1 (lake selection)	xx				
product 2 (fish sampling)	xxxxxxx		xxxxxxxxxx		
product 3 (water sampling/field meas.)	xxx		xxx		

A.1.f. Workprogram Update:

The sampling of 80 lakes for gamefish health and residue analyses, and water quality was completed as originally planned with some modifications:

Game Fish Sampling. Five of the 80 lakes (Crane, Kabetogama, Namakan, Rainy, and Sand Point) were sampled twice (1995 and 1996) in order to investigate variabilities associated with the date/season of sampling. The MDNR indicated it could not sample the following 5 lakes from the original plan: Big Moose (69-316), Fraser (38-372), Ge-Be-On-Equat (69-350), Horse (38-792), and Lac La Croix (69-224). In order to meet the legislative mandate of 80 lakes, 5 alternate lakes were sampled: Brule (16-348), Dumbell (38-393), Homer (16-406), Kawishiwi (38-080), and McDonald (16-235).

Water Quality Sampling. Water quality sampling has been completed for 80 lakes. Twenty-five of those lakes were sampled twice (spring and fall of 1996) in order to investigate variabilities associated with dates of sampling. The lake substitutions listed in "Game Fish Sampling" above, also apply to water quality sampling. In addition, though, early ice conditions forced additional lake substitutions for this sampling component. The following 4 lakes were not sampled due to early ice conditions: Adams (38-153), Hustler (69-343), Loon (69-470), and Oyster (69-330). The following 5 alternate lakes were sampled instead: Devilfish (16-029), Greenwood (16-077), Island (69-372), Superior (16-001), and Thomson (09-001).

A.2. Activity: Sample analyses.

A.2.a. Context within the project: Analyses results will quantify the condition parameters for each lake for 1995 and 1996.

A.2.b. Methods: Table 2 summarizes laboratory analyses that will be performed:

Mercury Analyses: Total mercury will be analyzed in fish, plankton, and water samples using cold vapor atomic absorption spectrometry (Perkin Elmer model 403 spectrometer) as the primary method and will involve methods reported by Glass *et al.* (1990, 1992) and Sorensen *et al.* (1990). All fish will be analyzed as individuals rather than composites. Water samples will be analyzed for methylmercury using phase ethylation (Liang *et al.*, 1994a, 1994b) followed by head space gas chromatography with atomic emission detection (HS-GC-AED, Hewlet Packard, 1993)

Selenium Analyses: Selenium content in selected fish will be determined using atomic absorption spectroscopy (Liang *et al.*, 1994c; Hemanutz *et al.*, 1992) using a Zeeman Perkin Elmer Model 5100, a head space and liquid injection gas chromatograph with atomic emission detection (HSLI-GC-AED, Hewlet Packard), or contract laboratory.

Selected heavy metals and chloro-organics: Selected heavy metals and chloro-organics will be analyzed using HSLI-GC-AED instrumentation.

Other Measurements. Turbidity and pH will be measured using Hatch and Radiometer meters, respectively. ANC will be determined by titration using Gran endpoint detection (Stumm and Morgan, 1981). Total organic carbon will be measured by infra-red absorbance. Details of the methods have been reported by us previously (Rapp *et al.*, 1985; Glass *et al.*; Eilers *et al.*, 1989)

Quality Assurance.
Selected samples analyzed for mercury using atomic absorption will be analyzed both with and without a deuterium arc background correction to check for false positive interferences in various sample types. Split samples will be provided to other interested investigators and archived by freezing for quality assurance checks and for future analysis of other components.

Accuracy of all measurements will be checked using spikes of known concentrations and NIST (National Institutes of Science and Technology) certified samples when available. Precision of all measurements will be checked by at least 10% replication of sample collection and 10% duplication of laboratory measurements.

Table 2. Summary of Laboratory Analyses to be Performed

	Parameter	Condition/Endpoint
Water Quality:	ANC	acid neutralizing capacity
	pH	acid condition
	electrical conductivity	dissolved solids/ionic strength
	turbidity	suspended solids/light penetration
	color	dissolved organic carbon/light penetration
	secchi disc	light penetration/trophic status
	total mercury	contaminant concentrations
	methylmercury[a]	contaminant concentrations
	total organic carbon[a]	contaminant source/transport
Fish[b]:	length and weight	fish size and condition

	age	maturity/growth rate/exposure time
	total mercury	contaminant concentrations
	selenium[a]	contaminant concentrations
	selected heavy metals[a]	contaminant concentrations
	selected chloro-organics[a]	contaminant concentrations
Plankton:	total mercury	contaminant concentrations

[a]selected samples.
[b]up to 10 fish of 1 or 2 species.

Check samples for quality assurance will be analyzed and portions will be archived for possible future analysis as part of the integrated program of research with other investigators from the state and universities.

Data Management: All raw data (e.g. instrument peak heights) will be recorded on strip chart, magnetic tape, and/or in bound notebooks with complete identification and safety. This is will be done to insure that any future questions regarding data quality can be addressed down to the original measurements. Master multiple copies of all original data will be kept in the possession of the principal investigators in UMD-assigned rooms.

A.2.c. Materials: Atomic absorption spectrometers (Perkin Elmer Corp. Model 403 and 5100), head-space gas chromatograph with atomic emission detector (Hewlet Packard), auto burette, pH meter, turbidity meter, colorimeter, balance, fluorimeter, reagents, syringes, water filtering apparatus, glassware.

A.2.d. Budget:
Total Biennial LCMR Budget: $50,000
LCMR Balance: $0

A.2.e. Timeline: 7/95 1/96 6/96 1/97 6/97
product 1 xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
(analyses of fish tissue and other biota)
product 2 xxx x xxx x
(analyses of water samples)

A.2.f. Workprogram Update:

Fish: All planned total mercury analyses, weight, and length measurements for the sampled game fish from 80 lakes have been completed. A total of 1,466 analyses on 1,063 fish (662 northern pike and 402 walleye). Egg and sperm from 24 fish (12 spawning pairs) were also analyzed. Additionally, approximately 275 analyses were made for the following methodological investigations relevant to previous (historical) sampling and analyses: ground vs. unground fish; skin-on vs. skin-off fillets; low vs. moderate fish digestion mass amounts; fish section variability; and interlab comparisons.

Of the 662 northern pike (from 53 lakes, averaging 12.5 per lake) analyzed for mercury, 118 (17.8%), 413 (62.4%), and 131 (19.8%) fish were found to be <160 ppb, 160-660 ppb, and >160 ppb, respectively. For the 402 walleye (from 46 lakes, averaging 8.7 per lake) analyzed for mercury, 124 (30.8%), 219 (54.5%), 59 (14.7%) fish were found in those same consumption advisory ranges.

Additional fish related data (from 80 lakes) were obtained from the MDNR: fish ages - 78 lakes; general survey data - 72 lakes; and stocking records - 48 lakes.

Preliminary data was presented to staff of the MPCA, MDNR, and MDH in St. Paul on January 7, 1997 and a preliminary comparison of present findings with historical results were sent to MPCA (E. Swain) on May 7, 1997 for comments.

Budgetary and time constraints precluded the analyses of selenium and additional heavy metals on selected fish. A follow-on proposal for additional work on these important samples is being prepared for consideration by the LCMR.

Water Quality: The following analyses have been completed for 80 lakes: ANC, pH, electrical conductivity, turbidity, color, sechhi disc depth, selected anions (sulfate, nitrate, chloride, fluoride, and phosphate), total organic carbon, and total mercury. Methyl mercury analyses have been completed for a selected subset of 26 lakes.

Plankton: Mercury analyses have been completed for 79 of 80 lakes.

B. Title of Objective/Outcome: Evaluate water quality and toxic contamination trends, ecological health, and watershed factors.

B.1. Activity: Create/quality assure 1995/1996 data base and assemble/quality assure historic data base.

B.1.a. Context within the project: Creation of the data base and assembling of the corresponding historic data base are necessary in order to proceed with an evaluation of contamination and water quality trends.

B.1.b. Methods: The 1995/1996 data base will be created on a Macintosh computer in Systat, Microsoft Excel, and Minitab software formats. Because of the strong dependence of mercury concentrations in fish and fish size parameters, mercury in fish data require some data reduction before data base entry of some critical parameters (Sorensen *et al.*, 1990). A non-linear regression of mercury concentrations against fish sizes (lengths, weights, and or ages) will yield a curve characteristic for each lake. Parameters defining these curves will be used to define the mercury concentrations at a standard fish size to allow comparisons among lakes and across time for a given fish species.

The data base will contain the following measured parameters: Individual fish mercury concentrations as well as those at standard lengths (northern pike 55 cm, walleye 39 cm; Sorensen *et al.*, 1990), weights, condition, and/or ages (including standard errors and number of fish); species; plankton mercury concentrations; lake plankton density; ANC; pH; turbidity; color; and trophic status (Secchi disc). Also included will be: 1) watershed, hydrologic, and lake morphometry parameters such as watershed area, precipitation, runoff, lake volume, lake area, lake renewal time, and location; 2) land cover parameters such as percent forest, water, and marsh cover; 3) and watershed land use descriptions such as urban development, mining, and forest cutting or burning; 4) and geologic descriptions of bedrock and soil type. These parameters will be derived from the ERL-D/UMD (Glass et al, 1985) Acid Deposition Gradient-Susceptibility Data base and updated where appropriate using data from state agency data bases (e.g. LMIC).

Quality Assurance. All data entry will be double checked for clerical errors. Suspect data will be identified through the following: 1) relational plots of all correlating parameters (e.g. conductivity and ANC); 2) field replicate and laboratory duplicate measurements; and 3) NBS and spike recoveries. All suspect data will be evaluated with respect to field and laboratory precisions and will be reanalyzed if unacceptable (e.g. residual > 3 x precision). Parameters of special interest will be analyzed by independent laboratories for additional data quality assurance.

Data bases will include a column used for error flags to identify items or data with special concerns or noteworthy comments.

Data Management: All synthesized data (e.g. analyte concentrations) will be assembled in columnar form with each row indicating sample type, date of sample collection, and lake name, identification number, and location. This data will be stored on computer disks and also printed in hard copy format. Master copies of this data base will be stored in UMD-assigned areas to ensure availability for future use. See Dissemination section for a discussion of how data will be accessed by others.

B.1.c. Materials: Use of Macintosh computer, statistical, spreadsheet, and word processing software, laser writer, floppy disks, and laboratory equipment (see A.2.c; for any reanalyses required).

B.1.d. Budget:

Total Biennial LCMR Budget: $60,000
LCMR Balance: $0

B.1.e. Timeline:	7/95	1/96	6/96	1/97	6/97
product 1 (assemble/quality assure historical data base)	xxxxxxxxxxxxxxxxxxxxx				
product 2 (create/quality assure 1995/1996 data base)	xxxxxxxx		xxxxxxx		
product 3 (reanalyze/evaluate suspect data)	xxx		xxx		

B.1.f. Workprogram Update:

The following are results of methodological investigations regarding mercury analyses in fish tissue. These are important in to comparing recent and historical data:

1) Precision, accuracy, and spike recoveries of recent mercury in fish data are given in Table 3.

Table 3. Summary of Precision, Accuracy, and Spike Recoveries for Fish Collected and Analyzed in 1995 and 1996.

	Accuracy†	Precision*		Spike
		unground	ground	Recovery
avg. value	99.5%	8.2%	7.5%	96%
std. dev.	8.7%	8.0%	6.6%	21%
std err	0.7%	0.7%	0.5%	2%
# samples	161	123	171	76

†DORM-1 dogfish certified standard.
*Both ground and unground tissue were run in duplicate.

2) Sixty-eight sections from a single fillet were analyzed to determine if there were any significant mercury concentration inhomogeneities throughout the flesh. The fillet was divided into 3 dimensions: center to skin; tail to front; and top to belly. Results showed that the only statistically significant divisions were among the tail to front sections.

3) Thirty-six northern pike and 28 walleye from several different lakes were analyzed by two different methods: as a fillet section without skin and as a ground fillet with skin (no scales). The ratios of with skin to without skin analyses were 0.88 (± 0.01 se) and 0.94 (± 0.02 se) for northern pike and walleye, respectively. The lower ratios with skin-on samples are because mercury concentrations in skin are much less than those in flesh. All analyses were converted to skin-on analyses for comparison purposes.

4) A subset of 20 fish from 3 lakes (Dumbell, Ball Club, and Saganaga) were analyzed by both the MNDNR and UMD in order to compare results between the two laboratories. A ratio (MDNR/UMD) of 0.89 (± 0.14 sd) for 20 fish was obtained.

Recent and historic mercury-in-fish data bases have been created/assembled and quality assured. All reanalyses of mercury concentrations in fish needed for this objective were completed. Data includes mercury concentration, length, and weight. Fish ages have not been quality assured yet as we still await age results for 2 lakes from the MnDNR. Final quality assurance of recent water quality data is not complete due to budget and time constraints.

An example of the type of data quality assurance needed to varify field measurements as compared with laboratory measurements is seen for the physical measurements of the sampled fishs' lengths and weights. These are important measurements, not only to characterize the demensions of the animal but also to determine the distribution of the Condition Factors (Beamish 1978) of the lake's fish population, Table 4.

Table 4. Summary of Relational QA between Field and Lab Measurements of Fish Lengths and Weights. These Measurements Are Used in the Determination of Fish Condition Factors.

Statistic	Lab/Field Ratios			
	Northern Pike		Walleye	
	length	weight	length	weight
avg =	96.6%	98.2%	97.3%	98.4%
stdev =	1.2%	3.7%	1.3%	3.6%
stderr =	0.05%	0.16%	0.07%	0.19%
n =	536	543	355	346

B.2. Activity: Evaluate water quality and toxic contamination trends and their relationships with watershed factors.

B.2.a. Context within the project: Results of this activity directly fulfills a stated objective of this project.

B.2.b. Methods: Statistical tests, t-test and single and multivariate regression analyses (Rapp *et al.*, 1985; Sorensen *et al.*, 1990), will be applied to the water quality and toxic contamination in fish data (1995/1996 vs historical) evaluate trends in terms of significance and rate of change. These computations will be done both on all lakes as a whole and on lake subsets grouped according to ranges of selected parameters such as ANC (Swain and Helwig, 1989) and color, which covary with mercury bioaccumulation. Various water quality, lake morphometry, hydrology, and watershed factors (i.e. forest cover, watershed area etc.) will be correlated against rates of change in water quality and mercury levels in fish. In addition, correlations among measurements described in Table 2 (except those measured on a selected basis) and watershed factors will be determined.

A preliminary examination of the historical data for the 70 lakes listed in Table 1 was conducted for the purpose of estimating the resolution one might generally expect for trend analyses of mercury concentrations in fish for those lakes. That is, what percent change in mercury concentration per year can one detect given the known uncertainties in the data? Results indicate that the average standard error of estimate for mercury concentrations of a standard size fish for each lake is approximately 20%. Also, the average year of sampling for that data is 1984. This means that the resolution of the fish contamination trend for an individual lake is typically no better than 2% per year (20% / 11 years). This figure might increase to roughly 3% per year when uncertainties in the 1995-1996 data are also considered.

The desired minimum mercury-in-fish contamination time trend resolution for this project is approximately 1%/yr. This number was chosen to be well below previous observations (see Section VII). Given this goal, the estimates above indicate: 1) Individual lake trend analyses should be reserved for lakes with better trend resolutions. Approximately 15 lakes listed in Table 1 may be adequate for this purpose. 2) When lakes are analyzed as a groups (delineated by water quality, watershed factors, etc) trend resolutions improve by approximately the square root of the number of lakes in the group. Groups of 9 lakes or more should typically give the desired time trend resolution. For a group of 70 lakes, the maximum time trend resolution for calculating changes in mercury concentrations could be better than 1/3 % per year .

Another aspect in data uncertainty is the differences in analytical methods between historical and present data. This will be minimized and evaluated by 1) utilizing the same techniques and equipment used in previous surveys, 2) analyzing the some fish using both methods in our laboratory, 3) reanalyzing some fish from the historical set that have been kept frozen since their first analysis, and 4) analyzing standard fish and tissue samples that have been certified by NIST.

All pertinent results will be reported using tables and/or graphs.

B.2.c. Materials: Use of , Macintosh computer, statistical and word processing software, laser writer, and floppy disks.

B.2.d. Budget:

Total Biennial LCMR Budget: $30,000

LCMR Balance: $0

B.2.e. Timeline:	7/95	1/96	6/96	1/97	6/97
product 1 (compute trends and statistical significances)				xxxxxxxx	
product 2 (relate trends to other parameters)				xxxxxxx	
product 3 (report results)					xxxxx

B.2.f. Workprogram Update:

Preliminary statistical methodology has been developed, tested, and comparisons between historical and recent data for mercury in fish concentrations have been made.

Regression Analyses. Regression statistics are developed for each fish species, lake, and sampling year in order to describe and compare the fish mercury (Hg) data. First, both fish mercury concentrations (ppb) and fish lengths (cm) are log transformed for two reasons: 1) transformed data are more normally distributed than untransformed data; and 2) the relationship between the mercury concentration and length is clearly non-linear for untransformed data whereas log transformation results in approximate linearity. The data are then described by computing the slope, intercept, number of data points, and the standard error of predicting any log[Hg concentration] given a log[length]. These statistical results, then, are the basic tools needed for evaluating differences in Hg concentrations between different sampling years or lakes.

A level of complexity arises in computing the regressions as a result of how the fish were composited for mercury analyses for much of the historical data. For some years it was a common practice to grind up several fish within a given size class and perform a single mercury analysis for the combined sample. Results from a composited sample, then, actually represents an average value for the number of fish represented. This translates into more statistical significance for a composited vs. non-composited sample. In general, each data point to be included in a regression may have different statistical power and, therefore, must be weighted appropriately. For our regression analyses we weighted each data point individually according to the number of fish in the ground into a single composite sample and analyzed.

Statistical Comparisons. In order to compare mercury concentration differences between, for example, two different sampling years for a given lake and fish species, we compare the log[Hg concentration] vs log[length] regression lines for each year. In general, the regression lines for the two sampling years being compared are not parallel and may even cross within the range of the data points. This means that any comparison between the two years will depend on the fish length at which the comparison is made. To evaluate the statistical significance of the predicted average log[Hg concentration] difference at a given length between the two sampling years being compared, we compute the t-statistic and the p-value (significance) for the difference. The t-statistic is a function of the difference between the predicted log[Hg concentration] values and the pooled standard errors of prediction for the two regression lines. The reported significances are for a 1-tail test.

For our treatment of the data, we generated plots of both t and p as a function of fish length. Presented in the figure tables are the lengths that are calculated for the critical significance points (90%, 95%, and 99%). Also shown are absolute and relative (%) mercury concentration differences (historical vs recent) that are computed for the mid-points of the length ranges representing a given level of statistical significance.

Results indicate that out of 75 study lakes (with sufficient historical data for statistical comparisons) 43 (57%) show less mercury levels for recent data while 19 (25%) and 16 (17%) show greater and the same levels, respectively. Of those lakes showing fish with less mercury, the average differences are 213 ng/g (36%) and 268 ng/g (30%), respectively, for northern pike and walleye. For those lakes showing more mercury, the average differences are -165 ng/g (-53%) and -165 ng/g (-72%), respectively, for northern pike and walleye. See attached report for summary figures and tables.

Mercury Effects on Reproductivity. Twelve northern pike spawning pairs (matched by size rank) were collected from 3 study lakes. Mercury concentrations and lengths for those fish ranged from, 172 - 2038 ng/g and 49.6 - 89.0 cm, respectively, for males and 213 - 1257 ng/g and 44.9 - 87.8 cm for females. It was found that mercury concentrations in sperm (average = 114 ng/g, range = 9 - 700 ng/g) were much higher (>10X) than in eggs (average = 10 ng/d, range 1 - 53 ng/g). The eggs were fertilized and incubated at the French River fish hatchery. Although no differences in egg hatch yield or fry behavior were observed, results were confounded by experimental conditions that were dictated by fish hatchery operations. For example, all incubation flasks were moved to another battery, resulting in thermal shock, to accommodate walleye hatching operations.

Water Quality and Related Trends. Preliminary statistical analyses comparing past and present measurements are in progress and results are expected within three months.

C. Title of Objective/Outcome: Synthesize, interpret, and report results for a 5-year mercury deposition data base.

C.1. Activity: Assemble/quality assure deposition data base.

C.1.a. Context within the project: Assembling deposition data base is necessary before data interpretations can be made.

C.1.b. Methods: Mercury deposition data (generated by UMD/ERL-D) from 8 sites located near Bethel, MN; Cavalier, ND; Duluth, MN; Ely, MN; Finland, MN; International Falls, MN; Lamberton, MN; and Raco, MI and covering the time period from 1990-1994 (some preliminary analyses for 1990-1992 given in Sorensen et al, 1994), using the methods described in Glass *et al.* (1991), will be combined with major ions data furnished by the MPCA and the National Atmospheric Deposition Program (see Glass and Loucks, 1986).

The data base will contain the following parameters with values listed for each weekly sample collection: sample date, precipitation depth, mercury concentration, mercury deposition, pH, conductivity, and concentrations/depositions of calcium, magnesium, potassium, sodium, ammonium, nitrate, chloride, and sulfate ions. All data will be assembled using Systat and Microsoft Excell formats on a Macintosh computer.

Quality Assurance. All data entry will be double checked for clerical errors. Suspect data will be identified through the following: 1) relational plots of all correlating parameters (e.g. conductivity and calcium concentration); 2) comparisons between the sums of cations and anions; 4) comparisons between calculated (Sorensen and Glass, 1987) and measured electrical conductivities; 3) field replicate and laboratory duplicate measurements (mercury concentrations); and 4) NIST and spike recoveries (mercury concentrations). Suspect data will be noted and possibly excluded from some analyses as deemed appropriate. The data bases will include a column used for error flags to identify items or data with special concerns or noteworthy comments.

Data Management: All data will be assembled in columnar form with each row indicating date of sample collection and location. This data will be stored on computer disks and also printed in hard copy format. Master copies of this data base will be stored in UMD-assigned areas to ensure availability for future use. See Dissemination section for a discussion of how data will be accessed by others.

C.1.c. Materials: Macintosh computer, statistical, spreadsheet, and word processing software, laser writer, floppy disks.

C.1.d. Budget:

Total Biennial LCMR Budget: $30,000
LCMR Balance: $0

C.1.e. Timeline:	7/95	1/96	6/96	1/97	6/97
product 1 (assemble/quality assure data base)	xxxxxxxxxxxxxxxxxxxxxxxx				

C.1.f. Workprogram Update:

Mercury deposition data for the 1990-1995 (5-yr) data base has been assembled and quality assurance for that component is complete. The addition of related data (e.g. major ions etc.) has not been completely assembled and quality assured due to budget and time constraints.

Extent of Study. From 1990 through 1995 we collected precipitation for monitoring total mercury deposition at 11 sites located in Minnesota, North Dakota, and Michigan (Figure 1). Six of those sites have 6 years of continuous weekly sampling data (Table I) which are the main focus of this report. Also presented are results of methylmercury measurements conducted in 1993 from 7 sites.

Table 1. Matrix of Mercury Monitoring Sites and Data Assembled and Quality Assured from 1990 to 1995[a]

	Location		Year					
Monitoring Site	Latitude	Longitude	90	91	92	93	94	95
Bethel, MN	46.1208	93.0042	T,I_1	T,I_1	T,I_1	T,m,I_1	T,m,I_1	T,m,I_1
Cavalier, ND	48.7825	97.7542	T,I_2	T,I_2	T,I_2	T,m,I_2	T,I_2	T,I_2
Duluth, MN	46.8403	92.0094	T	T	T,i_1	T,m,I_1	T,m,I_1	T,m,I_1
Ely, MN	47.9464	91.4961	T,I_2	T,I_2	T,I_2	T,m,I_2	T,I_2	T,m,I_2
Finland, MN	47.3875	91.1958	I_1	T,I_1	T,I_1	T,m,I_1	T,m,I_1	T,m,I_1
Int'l. Falls, MN	48.5917	93.1875	T,I_1	T,I_1	T,I_1	T,m,I_1	T,I_1	T,I_1
Lamberton, MN	44.2372	95.3006	T,I_2	T,I_2	T,I_2	T,m,I_2	T,I_2	T,I_2
Marcell, MN	47.5311	93.4686	I_2	I_2	I_2	I_2	I_2	t,I_2
Minneapolis, MN	44.9484	93.3438					t,m	T,m
Raco, MI	46.3742	84.7414	T,I_2	T,I_2	T,I_2	t,I_2	I_2	I_2
Tower, MN[b]	47.8033	92.4167				t	t	

[a]T - total Hg data; m - methyl Hg data; I_1 and I_2 - major ions and precipitation gauge data available from the Minnesota Pollution Control Agency and the National Atmospheric Deposition Program, respectively. Upper and lower case letters indicate data for full and partial year, respectively.

[b]Multiple week sampling periods for most Tower, MN data.

Extensive quality assurance measurements were made to verify precision and accuracy of precipitation sampling and mercury analysis methodology. Total mercury measurements in precipitation were performed by two independent methods of analysis in different laboratories. The results of these inter comparisons show that atomic absorption and fluorescence agree within 96 - 110 % of each other over the range 2 to 30 ng/L in precipitation samples.

C.2. Activity: Interpret data from the 5-yr deposition data base.

C.2.a. Context within the project: Results of this activity directly fulfills a stated objective of this project.

C.2.b. Methods: Concentrations and depositions of mercury and other deposition parameters will be examined over the 5-yr period of record. The influence of variable precipitation depths on mercury concentrations and depositions (Sorensen *et al.*, 1994) will be determined as part of the following specific goals.

Specific goals of this activity are:

1) Determine whether there are significant gradients or geographic patterns of mercury deposition.

This will involve the use of multivariate statistical techniques (Cole, 1969) such as factor analysis to discern patterns of covariation among sites. The factors obtained will then be used to determine whether the predominant patterns are associated with certain types of weather (e.g. thunderstorms vs cyclonic precipitation).

2) Determine empirical relationships that exist among depositional parameters.An appropriate form of empirical multivariate statistical analysis will be used to identify major patterns of covariance between mercury deposition and other deposition measurements (e.g. acid, ions, precipitation depth). An attempt will then be made to establish whether such patterns are related to sources or source regions. Source receptor relationships can be studied using: a) back-trajectory analysis (Glass *et al.*, 1991); b) an examination geographical variations of covarying parameters (specific or clustered events); and c) a comparison of covarying parameters with known characteristics of emission sources.

3) Determine the extent of temporal variabilityThis will involve characterizing any seasonal patterns and significant trends over the 5-yr period. Standard time series statistical analyses for individual stations, groupings of sites that correlate, and all sites as a whole will be used. These analyses can also be used to determine the temporal variation of the factors generated under specific goals 1) and 2) for this activity.

All pertinent results will be reported using tables and/or graphs.

C.2.c. Materials: Macintosh computer, statistical, spreadsheet, and word processing software, laser writer, floppy disks.

C.2.d. Budget:

Total Biennial LCMR Budget: $30,000

LCMR Balance: $0

C.2.e. Timeline:	7/95	1/96	6/96	1/97	6/97
product 1 (characterize deposition trends and statistical significances)			xxxxxxxxxxxxxxxxxxxx		
product 2 (characterize relationships among deposition ions and mercury)			xxxxxxxxxxxxxxxxxxxx		
product 3 (report results)					xxxxxxxx

C.2.f. Workprogram Update:

From 1990 through 1996 precipitation data were collected for total mercury wet deposition at 11 sites located in Minnesota, North Dakota, and Michigan . Six of those sites have 6 years of continuous weekly sampling data which are the main focus of this report. Also summarized are the results of methylmercury measurements conducted in 1993 from 7 sites. A draft manuscript summarizing the results (1990-1995) is being revised and will soon be submitted for journal peer review. See attached report for figures summarizing those results. Among the findings were the following:

1.) Precipitation monitoring was conducted weekly for six years at six sites (Bethel, MN; Cavalier, ND; Duluth, MN; Ely, MN; Int'l. Falls, MN; Lamberton, MN) located throughout Minnesota. The measurements included rain and snow fall volumes, and total and methyl mercury. Monitoring sites were named for the closest town or city. Other sites (Finland, MN; Marcell, MN; Minneapolis, MN; Raco, MI; Tower, MN) were also monitored for shorter durations.

2.) The total mercury deposition (micrograms per square meter) annual mean value was found to be 6.7 ±1.8 (S.D.), 6.9 ±1.4, 4.6 ±1.0, 7.3± 1.5, 8.6± 0.6, and 9.0± 2.5, respectively, for the years 1990-1996. Regression analysis for combined individual site annual average wet mercury deposition values versus time gives a significantly positive, non-zero slope of 0.55 $\mu g/m^2 yr$. Hg, ± 0.18 (S.E.). Data for each site are plotted and tabulated in the attached report.

3.) Further, a t-test statistical analysis showed the 3 northern most sites (Cavalier, Ely, and International Falls) were significantly lower ($p < 0.003$, 1 tail) in deposition than the other 3 sites (Bethel, Duluth, and Lamberton).

4.) Total mercury in precipitation is composed of approximately 2% methylmercury, the most toxic form. The methylmercury wet deposition correlates strongly with total mercury (+0.75), nitrate (+0.72), and sulfate (+0.78).

5.) Temporal comparisons (annually and quarterly) of mercury deposition, averaged across the six long-term sites, show the bulk of the mercury mass is deposited during the warmer rain season.

6.) Preliminary statistical analyses comparing mercury deposition and total coal consumption (Minnesota and border states) showed a relatively consistent annual pattern and a strong positive correlation.

VI. Evaluation:

The success of the project will be evaluated by 1) the completeness of a quality assured 1995/1996 water quality, toxic contamination of fish data, and ecological health base on electronic format for 80 Minnesota Lakes; 2) the completeness of a 5-yr mercury deposition data base merged with deposition data for major ions; 3) the presentation of definitive conclusions regarding trends of water quality, toxic contamination of fish, and the identification of possible watershed causal mechanisms; and 4) the presentation of definitive conclusions regarding time and regional trends of mercury deposition from 1990-1994 and relationships with depositions of other ions, emission sources and meteorological patterns.

An understanding of trends in water quality, toxic contamination of fish, ecological health, and mercury and major ion deposition will aid policy makers in assessing the urgency or degree of action for potential mitigative or regulatory options. A basis will also be provided for future judgment of the effectiveness of current policy decisions by comparing conditions measured at some future date with those measured in this project.

VII. Context within field:

In the later 1970s the discovery of mercury contaminated fish in 11 lakes within the Rainy Lake watershed prompted the Minnesota Department of Health to issue mercury consumption advisories for those water bodies. Because it was evident that no discharge sources could account for this contamination several questions arose such as: What was the source of mercury to these lakes? How long have they been contaminated? How many other lakes are contaminated? What caused some neighboring lakes to have significant differences in fish mercury levels?

In the early 1980s state agencies planned a lake sampling strategy designed to answer the question of how many lakes are contaminated. Initial findings indicated the problem was widespread in northeastern Minnesota and prompted continuing surveys which later included polychlorinated biphenyl (PCB) analyses for some lakes. To date 94% of the 454 Minnesota lakes and rivers sampled have fish consumption advisories for mercury or PCB (MDH, 1994).

Along with these surveys, research studies within the region documented relationships between mercury levels in fish and other factors such as fish size and some water quality/chemistry parameters which affect mercury bioaccumulation (Sorensen *et al.* 1990; Swain and Helwig, 1989; Helwig and Heiskary, 1985) and possible toxic impacts (Wiener and Spry, 1994). Other studies on bioaccumulation have found similar results in the United States (e.g. Wiener *et al.* 1990; Lathrop *et al.* 1989), Canada (e.g. Suns and Hitchin, 1990; Mcmurtry *et al.*, 1989) and Nordic countries (e.g. Lindqvist, 1991; Hakanson, 1980).

The link between water chemistry and mercury bioaccumulation in turn prompted some researchers to investigate mercury mitigation options based on the manipulation of water quality/chemistry. Some of these options included increasing the pH, covering or removing contaminated sediment, changing micronutrient levels, reducing vegetative growth, and addition of sequestering agents (e.g. Glass *et al.*, in prep.; Rudd and Turner, 1983a, 1983b; Paulsson and Lundburgh, 1991; Andersson and Borg, 1990; Gottofrey and Tjalve, 1990; Bongers *et al.*, 1977; and Jernelov *et al.*, 1975).

It was also discovered that the primary source of mercury to lakes and watersheds away from point source discharges is through atmospheric deposition (Nater and Grigal, 1992; Sorensen *et al.*, 1990). This source was also attributed to lake contamination problems observed in Sweden (Brosset, 1987). Following these findings, monitoring of mercury in precipitation at several sites in and around Minnesota began in 1990 and continues to date culminating in the collection of 5 years of weekly data.

The only attempt in answering the questions of how long the fish have been contaminated and what the current trends are in Minnesota was made by Swain and Helwig (1989). Using 14 lakes that were resampled about 7 years (average) apart it was found that mercury levels in fish were increasing at roughly 5% per year. Also, a comparison of mercury levels in fish from 6 lakes preserved from the 1930s and those taken in the 1970s showed an approximate 3% per year increase with time. These findings were consistent with studies which examined sediment strata in Minnesota (Swain *et al.*, 1992; Glass *et al.*, 1992) and elsewhere (Johansson, 1985; De Lacerda *et al.*, 1991) in that they all suggested that widespread mercury contamination occurred within the last 100 years.

If one estimates future fish mercury levels using these rate values (3 or 5%/yr), substantially different, though both alarming, results are obtained depending on the rate value used. The implications of such projections are important for policy makers in assigning priorities for potential regulatory or mitigative actions. However, because small numbers of lakes and a short time span of record (7 yrs for the 5%/yr figure) were all that were available for these rate estimates, subsequent use of these results in such decisions is limited.

This project workplan is designed to establish a firm foundation from which existing toxic contamination levels as well as water quality may be effectively compared to historic and future values. To do this, measurements will be done on a large number of lakes (80), that were previously surveyed in the 1970s and 1980s, so that more statistically significant and representative results will be obtained.

This project will also assess current water quality and toxic contamination trends and provide a more accurate determination of rates of change. These will stem from a comparison across a time span of about 10 to 20 years for these lakes.

In recognition of the importance of atmospheric deposition as the major source of mercury contamination to Minnesota lakes this project proposes to synthesize 5 years (1990-1994) of existing mercury in precipitation data. This data, compiled by UMD personnel, offers a unique opportunity to characterize regional and time (seasonal and yearly) trends. Also, because these data were collected in conjunction with other data (major ions) from other monitoring programs (NADP and MPCA), deposition relationships among various ions and mercury can be determined.

In Summary, all of the above components of the proposed study will contribute to 14 of the 20 research questions associated with mercury contaminations identified by the MPCA Mercury Task Force in June 1994 (MPCA, 1994). The specific questions this proposed project will directly or indirectly (in italics) address are as follows:

Watershed and Lake Processes

1) Do lakes with higher mercury in fish receive more mercury (from air and/or watershed)?
2) Do land-use changes increase mercury export from the watershed?
3) Is contamination increasing or decreasing?
4) Is the reproduction of wildlife, such as walleye and loon, impaired by mercury contamination?
5) Why do lakes vary greatly in mercury contamination of fish? What factors control foodchain bioaccumulation?
6) Where does mercury become methylated? (Emission source, air, watershed, wetlands, sediment, or lakewater?)
7) *Do sediment 'hotspots' cause elevated mercury in fish?*

Atmospheric Processes and Transport

1) Do lakes near emission sources receive significantly more mercury deposition?
2) How much geographic variability is there in mercury deposition?
3) Is deposition increasing or decreasing?
4) What atmospheric processes drive mercury deposition?
5) *What factors affect conversion of mercury from one form to another?*

Atmospheric Emissions

1) What are other regional sources that contribute to deposition in Minnesota?
2) Is methylmercury emitted by any sources?

Dr. George Rapp (Professor of Geology and Director of Archaeometry Laboratory, program manager), Dr. Gary Glass (Adjunct Professor of Geochemistry - Dept. of Geology, Member of Graduate Faculty and Adjunct Professor - Dept. of Biology, co-principle investigator), John Sorensen (Research Fellow, co-principal investigator), Dr. Stephen Hedman (Professor of Biology, Associate Dean of Graduate School, co-investigator), and Kent Schmidt (Research Fellow, research chemist) have all worked together on various mercury studies since 1987. These studies have involved mercury assessment and mechanisms research on over 100 Minnesota lakes, dozens of streams, and 8 precipitation monitoring sites with over 25,000 individual mercury analyses performed (total experience). Their findings have been important in areas such as mercury sources and bioaccumulation mechanisms. This work has been recognized by the Science Advisory Board of the USEPA in receiving a 1991 Scientific and Technological Award. Dr. Henry Cole, a Ph.D. meteorologist and co-investigator, has worked on mercury emission inventory and meteorological data bases for the interpretation of regulatory research objectives for EPA. He will advise and assist in obtaining needed data for research objectives.

Larry Kallemeyn's (Research Biologist for Voyageurs National Park, co-principal investigator) involvement with this project stems from the National Park Service's concern over high mercury concentrations in fish within Voyageurs National Park (VNP). Mr. Kallemeyn has been instrumental in assisting UMD in the study of mercury bioaccumlation mechanisms within VNP from 1991 to date and will assist in logistics of fish sampling, reproductive studies, effects assessments, and data interpretation.

VIII. Budget Context:

2-year period ending June 30, 1995: The UMD Graduate School and Departmental Awards are providing funds for the acquisition of instrumentation for measuring multi-element contaminant concentrations.
2-year period beginning July 1, 1995: LCMR funds only.

Transfer of funds by MPCA to UMD was delayed 6 months. Project period began 12/95.

IX. Dissemination:

Results of this project will be presented to Minnesota state agency staff and published in major peer-review journals. In addition, results will be distributed nationally and internationally as well as among the following agencies/institutions: Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, University of Minnesota-Duluth, U.S. Environmental Protection Agency, and Voyageurs National Park/National Biological Survey.

Data generated by this project will be reported to the MPCA in electronic format where it will be subsequently entered into STORET. Fish contamination data will be made available to the MDH for inclusion in their existing data base. Any new land use data generated by this project will be provided to the Land Management Information Center.

X. Time

Final reporting to LCMR by 3/31/98 with scientific journal article preparation extending through 6/30/98.

XI. Cooperation:

University of Minnesota, Duluth (UMD): UMD will lead in project management (Dr. George Rapp, Jr), with fish and water sampling, mercury and water chemistry analyses, quality assurance, and data interpretation managed by John Sorensen as a co-principal investigator. Dr. Gary Glass, Adjunct Professor of Geology and Biology will contribute personal time as needed to fulfill project needs. The Research Laboratory Building located on the lower campus of UMD will be used for project activities as needed. The Limnological Laboratory Building, (located near Lester River on Lake Superior), continues to be needed for office space, staging for field studies, sample storage and preparation, and storing supplies, equipment, and materials. It is assumed that all equipment presently in use by UMD personnel for mercury research will continue to be available for this project.

Environmental Research Laboratory-Duluth (ERL-D): This project continues to be of interest to EPA. Dr. Gary E. Glass, Senior Research Chemist at ERL-D will provide technical consultation for the project , 10% time. The original equipment used in the previous studies of water quality in the 1980's are needed to make the highest quality measurements and the strongest comparisons. The continued use of the space and equipment assigned to Dr. Glass are needed for this project to achieve the highest possible quality of science. In spite of the uncertainties being caused by the reorganization of EPA's Office of Research and Development, including the Duluth Lab., Dr. Glass has been assured by his EPA supervisor that he may conduct research on mercury effects, and also through Dr. Veith's (EPA Lab Director) assurance to Dr. Edward Swain(MPCA) that Dr. Glass could work on mercury effects research.

Voyageurs National Park (VNP)/National Biological Survey: VNP Research Biologist Larry Kallemeyn will serve as co-principal investigator for fish reproduction assessments and will coordinate all assistance from the VNP (up to 20% time). VNP will furnish some labor assistance for fish and water sample collection from lakes within the VNP and surrounding region. Assistance will also be provided by furnishing sampling equipment, a boat and motor and a cabin when possible.

Minnesota Department of Natural Resources (MDNR): The fisheries division staff from the MDNR will assist UMD in study lake selection, supervision of student field technicians and performing fish collection and measurements, and assessments of fish reproduction and population .

Minnesota Pollution Control Agency (MPCA): The MPCA air quality staff will act as the project coordinator and provide MPCA generated precipitation water chemistry data relevant to Objective C.

Contract Laboratories: Check and split samples will be analyzed as needed to further assure data quality.

XII. Reporting Requirements:

Semi-annual six-month work program update reports will be submitted not later than January 1, 1996, July 1, 1996, January 1, 1997, and a final six-month work program update and final report by ~~June 30~~ December 31, 1997.

XIII. Required Attachment:

Qualifications: See attached vitae and Project Staffing Summary.

XIV. Literature Cited:

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Mercury Deposition and Lake Quality Trends
Project: I-11 / I-15

Final Report
Draft Outline

to the
Legislative Commission on Minnesota Resources

December 1997

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Summary

Mercury Deposition Trends Study. From 1990 through 1996 precipitation data were collected for total mercury wet deposition at 11 sites located in Minnesota, North Dakota, and Michigan . Six of those sites have 6 years of continuous weekly sampling data which are the main focus of this report. Also summarized are the results of methylmercury measurements conducted in 1993 from 7 sites. A draft manuscript summarizing the results (1990-1995) is being revised and will soon be submitted for journal peer review. See attached report for figures summarizing those results. Among the findings were the following:

Precipitation monitoring was conducted weekly for six years at six sites (Bethel, MN; Cavalier, ND; Duluth, MN; Ely, MN; Int'l. Falls, MN; Lamberton, MN) located throughout Minnesota. The measurements included rain and snow fall volumes, and total and methyl mercury. Monitoring sites were named for the closest town or city. Other sites (Finland, MN; Marcell, MN; Minneapolis, MN; Raco, MI; Tower, MN) were also monitored for shorter durations.

The total mercury deposition (micrograms per square meter) annual mean value was found to be 6.7 ±1.8 (S.D.), 6.9 ±1.4, 4.6 ±1.0, 7.3± 1.5, 8.6± 0.6, and 9.0± 2.5, respectively, for the years 1990-1996. Regression analysis for combined individual site annual average wet mercury deposition values versus time gives a significantly positive, non-zero slope of 0.55 $\mu g/m^2$yr. Hg, ± 0.18 (S.E.). Data for each site are plotted and tabulated in the attached report.

Temporal comparisons (annually and quarterly) of mercury deposition, averaged across the six long-term sites, show the bulk of the mercury mass is deposited during the warmer rain season.

A t-test statistical analysis showed the 3 northern most sites (Cavalier, Ely, and International Falls) were significantly lower ($p < 0.003$, 1 tail) in deposition than the other 3 sites (Bethel, Duluth, and Lamberton).

Extensive quality assurance measurements were made to verify precision and accuracy of precipitation sampling and mercury analysis methodology. Total mercury measurements in precipitation were performed by two independent methods of analysis in different laboratories. The results of these inter comparisons show that atomic absorption and fluorescence agree within 96 - 110 % of each other over the range 2 to 30 ng/L in precipitation samples.

Total mercury in precipitation is composed of approximately 2% methylmercury, the most toxic form. The methylmercury wet deposition correlates strongly with total mercury (+0.75), nitrate (+0.72), and sulfate (+0.78).

Preliminary statistical analyses comparing mercury deposition and total coal consumption (Minnesota and border states) showed a relatively consistent annual pattern and a strong positive correlation.

Lake Quality Trends Study. A successful fish sampling program was completed for eighty Minnesota lakes by Department of Natural Resources regional staff personnel over the two year period, 1995-96. Eight to ten specimens from each lake were obtained and measured over a range of desired sizes. On this extensive collection of samples, more than 1,400 mercury analyses were performed to completely characterize the specimens and generate the necessary database needed to make quantitative comparisons with data obtained previously from the same lakes 3 to 20 years earlier. This extensive database constitutes a bench-mark concept in fish health and residue levels and is also useful in identifying the watershed factors which may be responsible for different degrees of fish condition as well as to determine mercury bioaccumulation mechanisms.

Mercury in Fish Comparisons. Comparisons of past and present data are complicated due to a number of different factors. Most commonly, data for each lake comparison was different in some respect: different numbers of fish, different dates of sampling, and different ways of analyzing the fish tissue. These factors were addressed to the extent possible and the resultant differences may, for the most part, represent actual changes in fish population mercury residue levels. Additional work is underway to understand more completely what these differences represent.

The results of our findings to date indicate that out of 75 study lakes (with sufficient historical data for statistical comparisons) 43 lakes (57%) show lower fish mercury levels for recent data compared to those reported previously, while 19 lakes (25%) show greater mercury concentrations, and 16 lakes (17%) show no significant difference.

Of those lakes having fish with less mercury, the average differences for northern pike are 213 ng Hg/g tissue (a 36% lower difference, on average) and for walleye are 268 ng Hg/g tissue (a 30% lower difference, on average).

For those lakes showing more mercury, the average differences for northern pike are 165 ng Hg/g tissue (a 53% higher difference, on average) and for walleye are 165 ng Hg/g tissue (a 72% higher difference, on average).

Since each lake is different with regard to the various factors influencing the comparisons, separate plots for each lake are provided showing the recent and historical mercury data, along with a more detailed explanation in the attached report.

Mercury Effects on Fish Fecundity. Twelve northern pike spawning pairs (matched by size rank) were collected from 3 study lakes. Mercury concentrations and lengths for those fish ranged from, 172 - 2038 ng/g and 49.6 - 89.0 cm, respectively, for males and 213 - 1257 ng/g and 44.9 - 87.8 cm for females. It was found that mercury concentrations in sperm (average = 114 ng/g, range = 9 - 700 ng/g) were much higher (>10X) than in eggs (average = 10 ng/g, range 1 - 53 ng/g). The eggs were fertilized and incubated at the French River fish hatchery. Although no differences in egg hatch yield or fry behavior were observed, the results may have been confounded by experimental conditions that were dictated by fish hatchery operations.

Water Quality and Related Trends. Preliminary statistical analyses comparing past and present measurements are in progress and results are expected within three months.

Introduction

In the later 1970s the discovery of mercury contaminated fish in 11 lakes within the Rainy Lake watershed prompted the Minnesota Department of Health to issue mercury consumption advisories for those water bodies. Because it was evident that no discharge sources could account for this contamination several questions arose such as: What was the source of mercury to these lakes? How long have they been contaminated? How many other lakes are contaminated? What caused some neighboring lakes to have significant differences in fish mercury levels?

In the early 1980s state agencies planned a lake sampling strategy designed to answer the question of how many lakes are contaminated. Initial findings indicated the problem was widespread in northeastern Minnesota and prompted continuing surveys which later included polychlorinated biphenyl (PCB) analyses for some lakes. According to the 1997 MDH Minnesota Fish Consumption Advisory (MDH 1997), a total of 687 lakes have received some degree of testing for mercury contamination in resident fish populations to date. Of those lakes tested only about 7% have no advisory restrictions. The other 93% of the lakes have advisories in categories (unlimited; 2 meals/week; 1 meal/week; 2 meals /month; 1 meal/month; and do not eat) which depend upon fish size and species and the type of person (e.g. children, women of child bearing age,...) as well as their annual fish eating habits. In addition, 77 locations on 46 rivers have been tested for either mercury or PCB concentrations in fish, resulting in advisories similar to that for lakes..

Along with these surveys, research studies within the region documented relationships between mercury levels in fish and other factors such as fish size and some water quality/chemistry parameters which affect mercury bioaccumulation (Sorensen *et al.* 1990; Swain and Helwig, 1989; Helwig and Heiskary, 1985) and possible toxic impacts (Wiener and Spry, 1994). Other studies on bioaccumulation have found similar results in the United States (e.g. Wiener *et al.* 1990; Lathrop *et al.* 1989), Canada (e.g. Suns and Hitchin, 1990; McMurtry *et al.*, 1989) and Nordic countries (e.g. Lindqvist, 1991; Hakanson, 1980).

The link between water chemistry and mercury bioaccumulation in turn prompted some researchers to investigate mercury mitigation options based on the manipulation of water quality/chemistry. Some of these options included increasing the pH, covering or removing contaminated sediment, changing micro nutrient levels, reducing vegetative growth, and addition of sequestering agents (e.g. Glass *et al.*, in prep.; Rudd and Turner, 1983a, 1983b; Paulsson and Lundburgh, 1991; Andersson and Borg, 1990; Gottofrey and Tjalve, 1990; Bongers *et al.*, 1977; and Jernelov *et al.*, 1975).

It was also discovered that the primary source of mercury to lakes and watersheds away from point source discharges is through atmospheric deposition (Nater and Grigal, 1992; Sorensen *et al.*, 1990). This source was also attributed to lake contamination problems observed in Sweden (Brosset, 1987). Following these findings, weekly monitoring of mercury in precipitation at several sites in and around Minnesota began in 1990 and continued, for the most part, until the end of 1995.

In 1989 Swain and Helwig attempted to answer the questions of how long Minnesota fish have been contaminated with mercury and what the current trends are. Using 14 lakes that were resampled about 7 years (average) apart it was found that mercury levels in fish were increasing at roughly 5% per year. Also, a comparison of mercury levels in fish from 6 lakes preserved from the 1930s and those taken in the 1970s showed an approximate 3% per year increase with time. These findings were consistent with studies which examined sediment strata in Minnesota (Swain *et al.*, 1992; Glass *et al.*, 1992) and elsewhere (Johansson, 1985; De Lacerda *et al.*, 1991) in that they all suggested that widespread mercury contamination occurred within the last 100 years.

If one estimates future fish mercury levels using these rate values (3 or 5%/yr), substantially different, though both alarming, results are obtained depending on the rate value used. The implications of such projections are important for policy makers in assigning priorities for potential regulatory or mitigative actions. However, because small numbers of lakes and a short time span of record (7 yrs for the 5%/yr figure) were all that were available for these rate estimates, subsequent use of these results in such decisions is limited.

This project was designed to establish a firm foundation from which existing toxic contamination levels as well as water quality may be effectively compared to historic and future values. To do this, measurements were done on a large number of lakes (80), that were previously surveyed in the 1970s and 1980s, so that more statistically significant and representative results could be obtained.

In recognition of the importance of atmospheric deposition as the major source of mercury contamination to Minnesota lakes we also synthesized 6 years (1990-1995) of existing mercury in precipitation data. This data, compiled by UMD personnel, offers a unique opportunity to characterize regional and time (seasonal and yearly) trends. Also, because these data were collected in conjunction with other data (major ions) from other monitoring programs (NADP and MPCA), deposition relationships among various ions and mercury can be determined.

Methods and Materials

1.1 Mercury Deposition Trends.

Sampling Methods. The wet deposition MIC and AreoChem samplers used in this study are shown in Figure 1.1 for the Duluth precipitation monitoring site. The sampling methodology used for the six-year precipitation sampling effort are described in detail in Sorensen et al. (1994). The data from the monitoring sites with the longest periods of record are presented below along with a description of the other sites studied within the 1990-95 time period.

Table 1. Matrix of Mercury-in-Precipitation Monitoring Sites and Data Assembled and Quality Assured from 1990 to 1995[a]

	Location		Year					
Monitoring Site	Latitude	Longitude	90	91	92	93	94	95
Bethel, MN	46.1208	93.0042	T,I_1	T,I_1	T,I_1	T,m,I_1	T,m,I_1	T,m,I_1
Cavalier, ND	48.7825	97.7542	T,I_2	T,I_2	T,I_2	T,m,I_2	T,I_2	T,I_2
Duluth, MN	46.8403	92.0094	T	T	T,i_1	T,m,I_1	T,m,I_1	T,m,I_1
Ely, MN	47.9464	91.4961	T,I_2	T,I_2	T,I_2	T,m,I_2	T,I_2	T,m,I_2
Finland, MN	47.3875	91.1958	I_1	T,I_1	T,I_1	T,m,I_1	T,m,I_1	T,m,I_1
Int'l. Falls, MN	48.5917	93.1875	T,I_1	T,I_1	T,I_1	T,m,I_1	T,I_1	T,I_1
Lamberton, MN	44.2372	95.3006	T,I_2	T,I_2	T,I_2	T,m,I_2	T,I_2	T,I_2
Marcell, MN	47.5311	93.4686	I_2	I_2	I_2	I_2	I_2	t,I_2
Minneapolis, MN	44.9484	93.3438					t,m	T,m
Raco, MI	46.3742	84.7414	T,I_2	T,I_2	T,I_2	t,I_2	I_2	I_2
Tower, MN[b]	47.8033	92.4167				t	t	

[a]T - total Hg data; m - methyl Hg data; I_1 and I_2 - major ions and precipitation gauge data available from the Minnesota Pollution Control Agency and the National Atmospheric Deposition Program, respectively. Upper and lower case letters indicate data for full and partial year, respectively.

[b]Multiple week sampling periods for most Tower, MN data.

Analyses Methods.

Precipitation Analyses. The analysis methodology for the six-year precipitation sampling effort given in Sorensen et al. (1994). Extensive quality assurance measurements were made to verify precision and accuracy of precipitation sampling and mercury analysis methodology.

2.1 Lake Quality Trends

Sampling Methods. The locations and names of the Minnesota lakes that were sampled for this project are shown in Figure 2.1.

Study lakes were selected based on the following considerations:

1) existence of fish populations and adequate historic fish residue analyses data.
2) existence of adequate historic water quality data. Important water quality measurements include pH, ANC, conductivity, color, and total organic carbon.

Concentrations of mercury in water, mercury in plankton, and major ions, as well as lake morphometry data, and watershed characteristics (e.g. land use, forest cover etc.) are also desirable.

3) availability of walleye or northern pike. These species are the two most commonly studied for mercury contamination are the focus of this effort. Game fish is preferred over forage fish for this project because there is more historical data for game fish and game fish are more mobile than forage fish and are, thus, better integrators of bioaccumulation variations across lake zones.

The available set of lakes that have sufficient historical data (100 - 200 lakes) for walleye or northern pike are listed by Helwig and Heiskary (1985) and MDNR (1994). The most comprehensive data available on water quality is available for 267 lakes (Rapp *et al.*, 1985). A comparison of these two sets revealed 70 lakes common to both. Because this project seeks to maximize statistical interpretations of mercury contamination and water quality trends, all 70 lakes were selected for this study.

Because most of the study lakes (70) are located in Minnesota Administrative Region 2 (MDNR, 1994), ten additional lakes were selected to provide a two-lake representation from each of the other five MNDNR Administrative Regions. Most of these lakes were studied previously for water quality characterization and acid deposition impacts (Rapp *et al.* 1985) and for mercury levels in water, sediment, plankton, and, in most cases, fish (analyzed by the Minnesota Department of Health) (Sorensen et. al. 1990).

A preliminary examination of the historical data for the 70 lakes from Region 2 was conducted for the purpose of estimating the resolution one might generally expect for trend analyses of mercury concentrations in fish for those lakes. That is, what percent change in mercury concentration per year can one detect given the known uncertainties in the data? Results indicate that the average standard error of estimate for mercury concentrations of a standard size fish for each lake is approximately 20%. Also, the average year of sampling for that data is 1984. This means that the resolution of the fish contamination trend for an individual lake is typically no better than 20% over 11 years. This figure might increase slightly when uncertainties in the 1995-1996 data are also considered.

The desired minimum mercury-in-fish contamination time trend resolution for this project is approximately 10%. This number was chosen to be well below previous observations (see Section VII). Given this goal, the estimates above indicate: 1) Individual lake trend analyses should be reserved for lakes with better trend resolutions. Approximately 15 lakes listed in Table 1 may be adequate for this purpose. 2) When lakes are analyzed as a groups (delineated by water quality, watershed factors, etc.) trend resolutions improve by approximately the square root of the number of lakes in the group. Groups of 9 lakes or more should typically give the desired time trend resolution.

Game Fish Sampling. Totals of 770 Northern pike and 552 walleye were sampled from 80 Minnesota lakes by the Minnesota Department of Natural Resources (MDNR) and by Voyageurs National Park personnel for lakes with in the VNP during 1995 and 1996. Fish were collected using gill and/or trap nets (MDNR 1993), tagged with and identification number, placed in a plastic bag, and kept in a cooler until transferred to the MNDNR or VNP local area headquarters where they were frozen. Fish were then sent by courier or 1-day parcel delivery to the University of Minnesota - Duluth Archaeometry Laboratory (UMD) where they were received frozen, logged in, and stored frozen until processing. Whole fish were received from the MNDNR while a single fillet from each fish was received from the VNP. On occasion, rotten specimens were received from the MNDNR. This was presumably a result of fish dying in the gill net sets before the nets were tended. Such specimens were noted.

For lakes containing both northern pike and walleye, a primary and secondary species of interest was assigned to match the available historical data. The goal was to collect at least 10 and 5 individual fish for each of the primary and secondary species, respectively. Another goal was to select fish lengths that were evenly distributed across the available pool of fish lengths sampled.

Fish weights and lengths and sex were determined in the field and also in the laboratory during processing. This provided a cross-check of fish identification. Laboratory processing included: scaling the fish (saving scale samples and cliethra for back-up aging); removing a fillet, slicing it in strips, and refreezing; grinding while frozen, and separately storing the bulk ground sample and a small aliquot (5-10 g) for analyses in zip-loc bags. Before grinding, a 5-10 g unground portion was removed from the fillet to be stored separately in a zip-loc bag. Smaller fish (less than 100 g) were diced with a knife instead of ground.

Five lakes were sampled in both study years in order to assess sampling variability.

Water Quality Sampling. Water quality sampling for 81 Minnesota lakes was accomplished in the fall of 1996 by UMD personnel. Twenty-five of those lakes were sampled twice (spring and fall of 1996) in order to investigate variabilities associated with dates of sampling. Because early ice conditions in 1996 prevented the sampling of four lakes studied for game fish contamination: Adams (38-153); Hustler (69-343); Loon (69-470); and Oyster (69-330)), the following 5 alternate lakes were sampled instead: Devilfish (16-029); Greenwood (16-077); Island (69-372); Superior (16-001); and Thomson (09-001).

Field measurements and sampling were conducted in a deep portion (not necessarily the deepest) of the lake. The following field measurements were made: a profile (surface, mid-depth, and bottom) of conductivity and temperature using a Yellow Spring Instrument Co. (YSI) model 32 meter; depth to bottom using a Hummingbird Wide 100 depth indicator; and secchi depth. Location was documented by recording the position coordinates using a global positioning system (GPS, Garmin) instrument and by taking photographs.

The water sample obtained for mercury analysis was taken using a 250-mL polyethylene bottle containing a preservative (6 mL of 25% HNO_3 and 2.5% K_2CrO_7). A second 250-mL bottle held by a stainless steel weight was used to collect the sample, from about a 1-m depth, which was poured into the bottle containing the preservative. After sampling, the bottle was capped, mixed by shaking, and sealed in two ziplock bags for protection against contamination. Next a 1-L water bottle, used for collecting samples for basic water chemistry analyses, was rinsed two times with approximately 200 mL lake water and filled with four successive grabs (1-m depth).

Plankton was be sampled using a Wisconsin style net (Wildco Wildlife Supply Co.) and a Minnesota plankton bucket (J. Shapiro, U. of Minnesota, Mpls, MN). The stop valve at the bottom of the Minnesota bucket was opened and the entire net/bucket was rinsed in the lake four times. The stop valve was then closed and the net was lowered to the desired depth. The net was raised at a constant rate of approximately 1 m/s to the surface whereupon it was rinsed in the lake approximately four times to wash the plankton from the net into the bucket. Tows were repeated until sufficient plankton biomass for Hg analysis was obtained. This generally required a total tow length of 30 m, however, visual inspection of the sample often indicated that sufficient plankton was present to allow a shorter tow length.

Plankton was transferred to a 250-mL sample bottle (with preservative) by first holding the bucket/net net at approximately 60 degrees for draining. The plankton bucket was then placed into the mouth of the sample bottle and the stop valve was opened allowing residual lake water (~20 mL) plus plankton to be collected. Next, the top portion of the bucket and net were removed and the plankton were rinsed from the bucket's 80 µm net with ~200 mL DIW. The sample bottle was capped, stored inside two ziplock bags and placed into the cooler. The Minnesota bucket and net were reassembled and rinsed, with the stop valve open, four times in the lake and stored in a ziplock bag. Further discussion on plankton sample is given in Sorensen *et al.* (1990). It was discovered on that the one-way check-valve for the Minnesota bucket was not in place for samples taken before 6/13/96. This should not affect the ability to measure mercury in the plankton but may influence estimates of biomass for those samples. A separate experiment with and without the check valve was performed to assess the difference in sampling results.

All samples were taken while wearing latex gloves and were kept near 4°C during transit and storage until analyzed. Two sets of field measurements and samples were taken for every 10th lake to assess sampling variability. All field measurements and sample history were be recorded in standard bound notebooks in the field. Each entry includes the date of sampling, the assigned site number, the geographic position of the site, field measurements, and the names of the technicians performing the sampling. Any sampling problems that may cause sample contamination or affect the sample integrity were recorded in the field notebook as well as reported to the project manager upon return from the field. Logbooks are archived in a designated area at the Archaeometry/ Laboratory at UMD.

Fish Fecundity Assessment. Three Northern Minnesota lakes were chosen to be studied for effects of mercury contamination on the spawning success of northern pike. For this study, five adult spawning pairs were taken from both Kabetogama and Crane lakes while two pair were taken from for Namakan Lake. These fish were collected by VNP personnel who used trap nets placed in selected regions of the lakes. The Pike were stripped of their spawn, cut into fillets, and delivered to UMD. The milted eggs were then transported within a 12 hour period to the MNDNR French River Fisheries to be placed in incubators. Separate samples of sperm and eggs were taken from each fish for mercury analyses. The temperature of the eggs were monitored during the trip in order to keep them within the desired temperature limit of 8.8 to 11.1°C.

The cylindrical incubators provided by the MNDNR were 43.2 cm height with a diameter of 48.0 cm. Water from the Lester River entered through a tube at the bottom of each incubator and exited through another tube at the top which contained a screen to prevent the transfer of eggs out of the incubator.

During the incubation, the flow rate and condition of the eggs were monitored on a daily basis while the temperature of the flow stream was continuously logged by a computer. The temperatures were also taken manually using a hand-held thermometer each morning. Daily maintenance included: noting the condition of the eggs, the number of dead fungused eggs, and how well the eggs were rolling within the incubators; removal (siphoning off) of dead eggs; and cleaning debris from the outlet tube screen.

To keep the eggs from gelling together, the river water was treated with a low concentration of formalin at given intervals. The formalin was only used up until the eggs hatched. When the eggs hatched, the temperature and date was annotated in the log book and an estimation of the number of hatched fry was made by visual inspection. The behavior of the fry was also noted in the log book. Within a 24 hour period, most of the fertile eggs hatched. The live fry within the incubator were then removed in order to clear the remaining fungused eggs and debri from the bottom.

As the fry matured, their physical characteristics as well as their behavior, was recorded daily, noting significant changes that occurred. Photos were also taken of these fry at various stages of development. After 10 days of development as yolksac fry, two samples of 50 fry were taken from each incubator, placed in zip-loc bags, and transported to UMD for analyses and storage.

Analyses Methods

Mercury Analyses. Total mercury was analyzed in fish (including egg and sperm), plankton, and water samples using cold vapor atomic absorption spectrometry (Perkin Elmer model 403 spectrometer) using methods reported by Glass *et al.* (1990, 1992) and Sorensen *et al.* (1990). All fish were analyzed as individuals rather than composites. A subset of water samples were analyzed for methylmercury using phase ethylation (Liang *et al.*, 1994a, 1994b) followed by fluorescence detection

Approximately 275 analyses were made for the following methodological investigations relevant to previous (historical) sampling and analyses: ground vs. unground fish; skin-on vs. skin-off fillets; low vs. moderate fish digestion mass amounts; fish section variability; and interlab comparisons.

Accuracy of all mercury measurements was checked using spikes of known concentrations and NIST (National Institutes of Science and Technology) certified samples when available. Laboratory precision was checked by analyzing at least 10% of all samples in duplicate.

Historical Fish Analyses. The overwhelming majority of historical fish analyses were done using ground fillet wth skin (after scaling). In many instances fish of similar size were composited before analyzing for mercury. These cases were all noted and subsequent data synthesis of such data takes this into account. Fish collected from 1979-1984 were analyzed for mercury by the MDH, those collected from 1985-1986 were analyzed in conjunction with the MDH but with methods not given, and those collected from 1987-1992 were analyzed by Braun Intertec in conjunction with the MNDNR.

Fish Aging. Fish ages were determined by the various MNDNR area offices and VNP personnel that collected the fish. Annular lines on scales was the primary method, however, VNP personnel used cliethra for aging northern pike.

Water Quality Measurements. Water samples were analyzed for conductivity, pH and gran alkalinity using a 50-mL aliquot of each sample heated to 25°C in a warm water bath. A separate aliquot was analyzed for apparent color and turbidity. Details of the methods have been reported by us previously (Rapp *et al.*, 1985; Glass *et al.*; Eilers *et al.*, 1989)

Conductivity. Electric conductivity was determined with a Radiometer CDM83 meter a PP1042 conductivity electrode and a T801 temperature probe (Radiometer America Inc., Westlake, OH).

pH. pH was determined using a Radiometer pHM63 meter with a Radiometer G2401C combination electrode. The meter was calibrated using 6.86 and 4.01 buffers according to the manufacturer's instructions.

Alkalinity. Alkalinity titrations were performed on a Radiometer DTS 800 series digital titration system. Components included a pHM63 pH meter, G2401C combination electrode, an ABU80 autoburette with a 10 mL burette, a TTA60 ttitration assembly, and a TTT81 digital titrator with TIK801 titrator keyboard. Keyboard settings of Stability 5, mode 0.3, and an endpoint pH of 3.5 were utilized. After the initial pH was determined the sample was fortified with 0.050 mL of 1.0 N KCl and titrated with 0.0200 N H_2SO_4. The titrant was standardized with 1 mL of Na_2CO_3 (2.638g/L) in duplicate at the start of each days titrations. Gran alkalinity was calculated using the Method of Kramer using the data points from pH 4.5 to 3.5 (Stumm and Morgan, 1981). Alkalinity is reported as µeq HCO_3^-/L.

Color. Color was measured using the colorimetric platinum-cobalt method on a Hellige Aqua Tester using 0-25, 0-50, 0-75 and 0-100 range color wheels. Samples were shaken to resuspend any particulate material, poured into the colorimeter tube and measured at ambient temperature. Samples with color >100 Pt-Co units were diluted into range and the color obtained was multiplied by the dilution factor. An aliquot of sample was filtered through milipore 0.7 µm glass filters and filtered color was determined.

Turbidity. Nephelometric turbidity was measured at ambient temperature using a Hach 2100A Turbidimeter. Samples were shaken , the cell was filled and turbidity was determined after 3 min equilibration.

Fish Regression Analyses. Because of the strong dependence of mercury concentrations in fish and fish size, mercury in fish data require some data reduction before interpretation (Sorensen *et al.*, 1990). A non-linear regression of mercury concentrations against fish length yields a curve characteristic for each lake. Regression statistics are developed for each fish species, lake, and sampling year in order to describe and compare the fish mercury (Hg) data. First, both fish mercury concentrations (ppb) and fish lengths (cm) are log transformed for two reasons: 1) transformed data are more normally distributed than untransformed data; and 2) the relationship between the mercury concentration and length is clearly non-linear for untransformed data whereas log transformation results in approximate linearity. The data are then described by computing the slope, intercept, number of data points, and the standard error of predicting any log[Hg concentration] given a log[length]. These statistical results, then, are the basic tools needed for evaluating differences in Hg concentrations between different sampling years or lakes.

A level of complexity arises in computing the regressions as a result of how the fish were composited for mercury analyses for much of the historical data. For some years it was a common practice to grind up several fish within a given size class and perform a single mercury analysis for the combined sample. Results from a composited sample, then, actually represents an average value for the number of fish represented. This translates into more statistical significance for a composited vs. non-composited sample. In general, each data point to be included in a regression may have different statistical power and, therefore, must be weighted appropriately. For our regression analyses we weighted each data point individually according to the number of fish in the ground into a single composite sample and analyzed.

Statistical Comparisons. In order to compare mercury concentration differences between, for example, two different sampling years for a given lake and fish species, we compare the log[Hg concentration] vs log[length] regression lines for each year. In general, the regression lines for the two sampling years being compared are not parallel and may even cross within the range of the data points. This means that any comparison between the two years will depend on the fish length at which the comparison is made. To evaluate the statistical significance of the predicted average log[Hg concentration] difference at a given length between the two sampling years being compared, we compute the t-statistic and the p-value (significance) for the difference. The t-statistic is a function of the difference between the predicted log[Hg concentration] values and the pooled standard errors of prediction for the two regression lines. The reported significances are for a 1-tail test.

For our treatment of the data, we generated plots of both t and p as a function of fish length. Presented in the figure tables are the lengths that are calculated for the critical significance points (90%, 95%, and 99%). Also shown are absolute and relative (%) mercury concentration differences (historical vs recent) that are computed for the mid-points of the length ranges representing a given level of statistical significance.

All computations were made on a Macintosh computer using Excel and Systat software.

Outline of Results

1.1 Mercury Deposition Trends.

From 1990 through 1996 precipitation data were collected for total mercury wet deposition at 11 sites located in Minnesota, North Dakota, and Michigan . Six of those sites have 6 years of continuous weekly sampling data which are the main focus of this report. Also summarized are the results of methylmercury measurements conducted in 1993 from 7 sites. A draft manuscript summarizing the results (1990-1995) is being revised and will soon be submitted for journal peer review. See attached report for figures summarizing those results. Among the findings were the following:

Precipitation monitoring was conducted weekly for six years at six sites (Bethel, MN; Cavalier, ND; Duluth, MN; Ely, MN; Int'l. Falls, MN; Lamberton, MN) located throughout Minnesota using the equipment shown in Figure 1. The measurements included rain and snow fall volumes, and total and methyl mercury. Monitoring sites were named for the closest town or city. Other sites (Finland, MN; Marcell, MN; Minneapolis, MN; Raco, MI; Tower, MN) were also monitored for shorter durations.

The total mercury deposition (micrograms per square meter) annual mean value was found to be 6.7 ±1.8 (S.D.), 6.9 ±1.4, 4.6 ±1.0, 7.3± 1.5, 8.6± 0.6, and 9.0± 2.5, respectively, for the years 1990-1996. Regression analysis for combined individual site annual average wet mercury deposition values versus time gives a significantly positive, non-zero slope of 0.55 $\mu g/m^2 yr$. Hg, ± 0.18 (S.E.). Data for each site are tabulated in Table 1 and plotted in Figure 2 as annual averages, showing the relationships among sites and between years.

Temporal comparisons (annually and quarterly) of mercury deposition are shown in Figure 3, averaged across the six long-term sites, show the bulk of the mercury mass is deposited during the warmer rain season.

A t-test statistical analysis showed the 3 northern most sites (Cavalier, Ely, and International Falls) were significantly lower ($p< 0.003$, 1 tail) in deposition than the other 3 sites (Bethel, Duluth, and Lamberton). This is illustrated further in Figure 4 where the cumulative weekly wet mercury deposition values are shown beginning from Jan. 1 1990. The final error bars indicate significant accumulation differences between monitoring sites.

Extensive quality assurance measurements were made to verify precision and accuracy of precipitation sampling and mercury analysis methodology. Total mercury measurements in precipitation were performed by two independent methods of analysis in different laboratories. The results of these inter comparisons show that atomic absorption and fluorescence agree within 96 - 110 % of each other over the range 2 to 30 ng/L in precipitation samples as shown in Figure 5.

Total mercury in precipitation is composed of approximately 2% methylmercury, the most toxic form. Methylmercury wet deposition correlates strongly with total mercury (+0.75), nitrate (+0.72), and sulfate (+0.78).

Preliminary statistical analyses comparing mercury deposition and total coal consumption (Minnesota and border states) showed a relatively consistent annual pattern and a strong positive correlation.

2.1 Lake Quality Trends.

Fish Bench-Mark Database. A successful fish sampling program was completed for eighty Minnesota lakes by Department of Natural Resources regional staff personnel over the two year period, 1995-96. Eight to ten specimens from each lake were obtained and measured over a range of desired sizes. On this extensive collection of samples, more than 1,400 mercury analyses were performed to completely characterize the specimens and generate the necessary database needed to make quantitative comparisons with data obtained previously from the same lakes 3 to 20 years earlier. This extensive database constitutes a bench-mark concept in fish health and residue levels and is also useful in identifying the watershed factors which may be responsible for different degrees of fish condition as well as to determine mercury bioaccumulation mechanisms.

A total of 1,466 mercury analyses on 1,063 fish (662 northern pike and 402 walleye) were made. Egg and sperm from 24 fish (12 spawning pairs) were also analyzed.

Of the 662 northern pike (from 53 lakes, averaging 12.5 per lake) analyzed for mercury, 118 (17.8%), 413 (62.4%), and 131 (19.8%) fish were found to be <160 ppb, 160-660 ppb, and >160 ppb, respectively (Table 2.1, Figure 2.2). For the 402 walleye (from 46 lakes, averaging 8.7 per lake) analyzed for mercury, 124 (30.8%), 219 (54.5%), 59 (14.7%) fish were found in those same consumption advisory ranges.

Statistical results (Table 2.2, Figure 2.3) indicate that for 75 of 80 study lakes (those with sufficient historical data for statistical comparisons) 43 (57%) show less mercury levels for recent data while 19 (25%) and 16 (17%) show greater and the same levels, respectively. Of those lakes showing fish with less mercury, the average differences are 213 ng/g (36%) and 268 ng/g (30%), respectively, for northern pike and walleye. For those lakes showing more mercury, the average differences are -165 ng/g (-53%) and -165 ng/g (-72%), respectively, for northern pike and walleye. See attached report for summary figures and tables.

The following are results of methodological investigations regarding mercury analyses in fish tissue.

1) Precision, accuracy, and spike recoveries of recent mercury in fish data are given in Table 2.3.

Table 2.3. Summary of Precision, Accuracy, and Spike Recoveries for Fish Collected and Analyzed in 1995 and 1996.

	Accuracy†	Precision*		Spike Recovery
		unground	ground	
avg. value	99.5%	8.2%	7.5%	96%
std. dev.	8.7%	8.0%	6.6%	21%
n	161	123	171	76
std err	0.7%	0.7%	0.5%	2%

†DORM-1 dogfish.

*Both ground and unground tissue were run in duplicate.

2) Sixty-eight sections from a single fillet were analyzed to determine if there were any significant mercury concentration inhomogeneities throughout the flesh. The fillet was divided into 3 dimensions: center to skin; tail to front; and top to belly. Results showed that the only statistically significant divisions were among the tail to front sections.

3) Thirty-six northern pike and 28 walleye from several different lakes were analyzed by two different methods: as a fillet section without skin and as a ground fillet with skin (no scales). The ratios of with skin to without skin analyses were 0.88 (± 0.01 se) and 0.94 (± 0.02 se) for northern pike and walleye, respectively. The lower ratios with skin-on samples are because mercury concentrations in skin are much less than those in flesh. All analyses were converted to skin-on analyses for comparison purposes.

4) A subset of 20 fish from 3 lakes (Dumbell, Ball Club, and Saganaga) were analyzed by both the MNDNR and UMD in order to compare results between the two laboratories. A ratio (MDNR/UMD) of 0.89 (± 0.14 sd) for 20 fish was obtained.

An example of the type of data quality assurance needed to verify field measurements as compared with laboratory measurements is seen for the physical measurements of the sampled fishs' lengths and weights. These are important measurements, not only to characterize the dimensions of the animal but also to determine the distribution of the Condition Factors (Beamish 1978) of the lake's fish population, Figure 2.4.

It was discovered that a fish lengths and weights measured in the field are slightly larger than those observed in the lab (Table 2.4). This occurred even for those fish that were not examined for sex in the field. We attribute the small difference to the freeze-thaw cycle that occurs before laboratory measurements are made.

Table 2.4. Summary of Relational QA between Field and Lab Measurements of Fish Lengths and Weights. These Measurements Are Used in the Determination of Fish Condition Factors.

Statistic	Lab/Field Ratios			
	Northern Pike		Walleye	
	length	weight	length	weight
avg =	96.6%	98.2%	97.3%	98.4%
stdev =	1.2%	3.7%	1.3%	3.6%
n =	536	543	355	346
stderr =	0.05%	0.16%	0.07%	0.19%

Additional fish survey related data were obtained from the MDNR (and VNP for aging): fish ages - 78 lakes; general survey data - 72 lakes; and stocking records - 48 lakes. These data have been received but not compiled and analyzed.

Fish Fecundity Assessment. Mercury concentrations and lengths for the 12 spawning fish pairs ranged from 172 - 2038 ng/g and 49.6 - 89.0 cm, respectively, for males and 213 - 1257 ng/g and 44.9 - 87.8 cm for females. It was found that mercury concentrations in sperm (average = 114 ng/g, range = 9 - 700 ng/g) were much higher (>10X) than in eggs (average = 10 ng/d, range 1 - 53 ng/g). The eggs were fertilized and incubated at the French River fish hatchery. Although no differences in egg hatch yield or fry behavior were observed, results were confounded by experimental conditions that were dictated by fish hatchery operations. For example, all incubation flasks were moved to another battery, resulting in thermal shock, to accommodate walleye hatching operations.

Water Quality and Related Trends. Preliminary statistical analyses comparing past and present measurements are in progress and results are expected within three months.

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Tables and Figures for Mercury Deposition Trends Study.

Table 1.1. Statistical Summary of Mercury Concentrations, Wet Mercury Depositions, and Precipitation Depths from 1990-1995 for Long-Term Monitoring Sites in Minnesota.

Site	1990			1991			1992		
	Vol Wtd Conc. (ng/L)	Depos (ug/m2)	Precip. Depth (cm)	Vol Wtd Conc. (ng/L)	Depos (ug/m2)	Precip. Depth (cm)	Vol Wtd Conc. (ng/L)	Depos (ug/m2)	Precip. Depth (cm)
Bethel	10.41	9.35	90.40	7.44	7.93	106.69	9.01	4.69	54.60
Cavalier	15.06	5.26	34.90	12.40	7.28	58.68	9.31	3.85	41.36
Duluth	10.17	7.83	77.02	9.56	8.30	86.83	8.73	5.83	66.76
Ely	8.10	5.37	66.35	7.32	4.98	68.02	5.13	3.16	61.61
IFalls	7.85	4.77	60.83	7.49	5.31	70.89	8.50	5.06	59.61
Lamberton	11.97	7.40	61.80	10.44	7.70	73.80	7.56	5.06	66.99
mean =	10.59	6.66	65.22	9.11	6.92	77.49	8.04	4.61	58.49
std dev =	2.68	1.81	18.57	2.07	1.42	16.97	1.54	0.96	9.59

Site	1993			1994			1995		
	Vol Wtd Conc. (ng/L)	Depos (ug/m2)	Precip. Depth (cm)	Vol Wtd Conc. (ng/L)	Depos (ug/m2)	Precip. Depth (cm)	Vol Wtd Conc. (ng/L)	Depos (ug/m2)	Precip. Depth (cm)
Bethel	9.43	8.73	95.82	12.70	8.78	70.56	10.67	9.42	93.36
Cavalier	9.96	6.18	62.03	17.49	8.24	47.08	21.67	12.68	58.50
Duluth	9.48	7.19	75.81	12.80	9.03	70.55	11.58	10.11	87.29
Ely	9.02	6.22	68.95	11.20	7.78	69.45	10.07	5.77	57.31
IFalls	9.45	5.89	62.33	11.92	8.46	70.95	10.23	6.40	62.59
Lamberton	9.94	9.47	95.21	15.92	9.45	59.39	13.89	9.49	68.30
mean =	9.55	7.28	76.69	13.67	8.62	64.66	13.02	8.98	71.23
std dev =	0.35	1.49	15.43	2.47	0.60	9.68	4.46	2.54	15.41

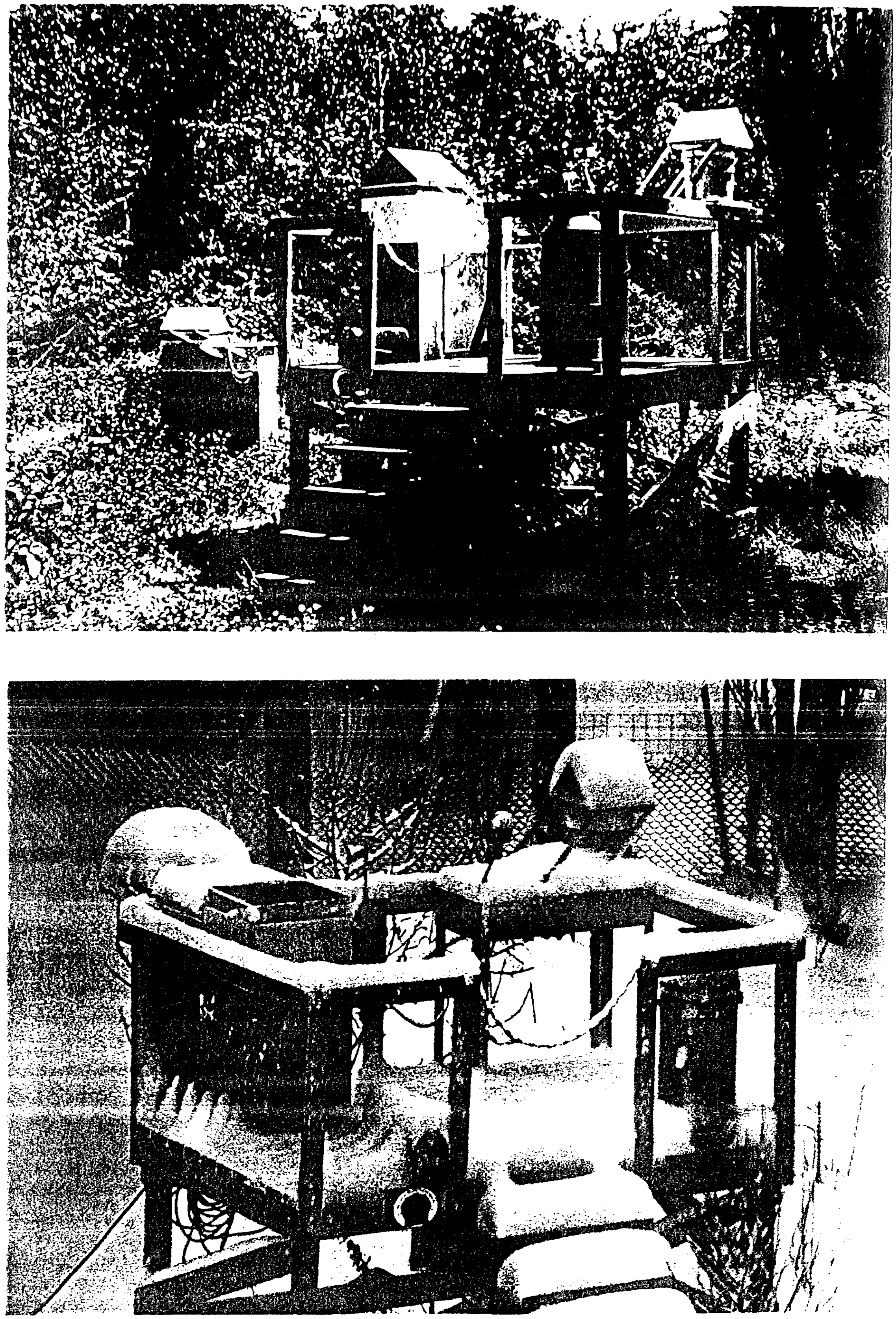


Figure 1.1. Precipitation monitoring site at Lester Park, Duluth, MN, showing various sampling equipment and monitoring instruments in summer and winter (photos by G. E. Glass).

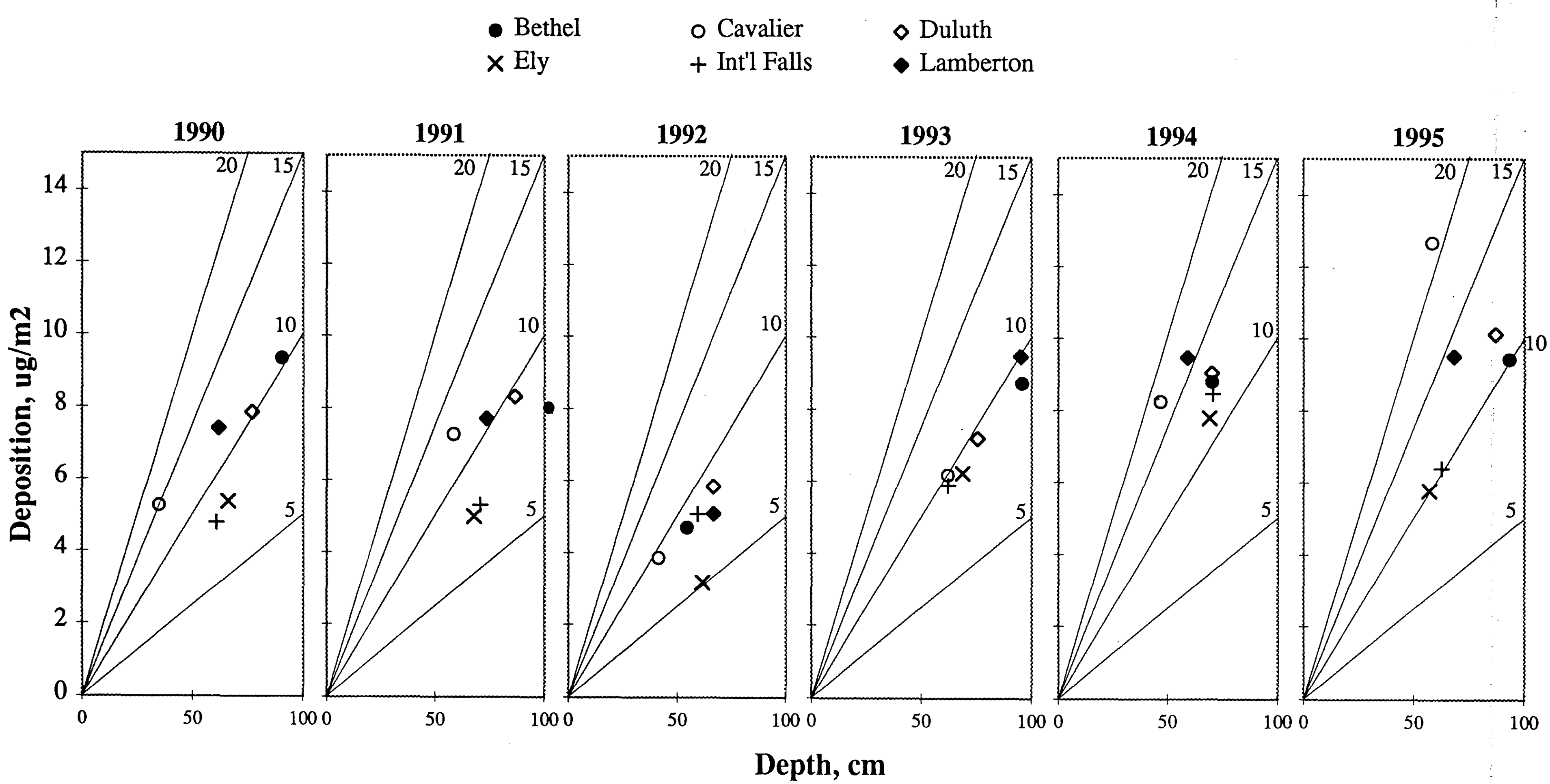
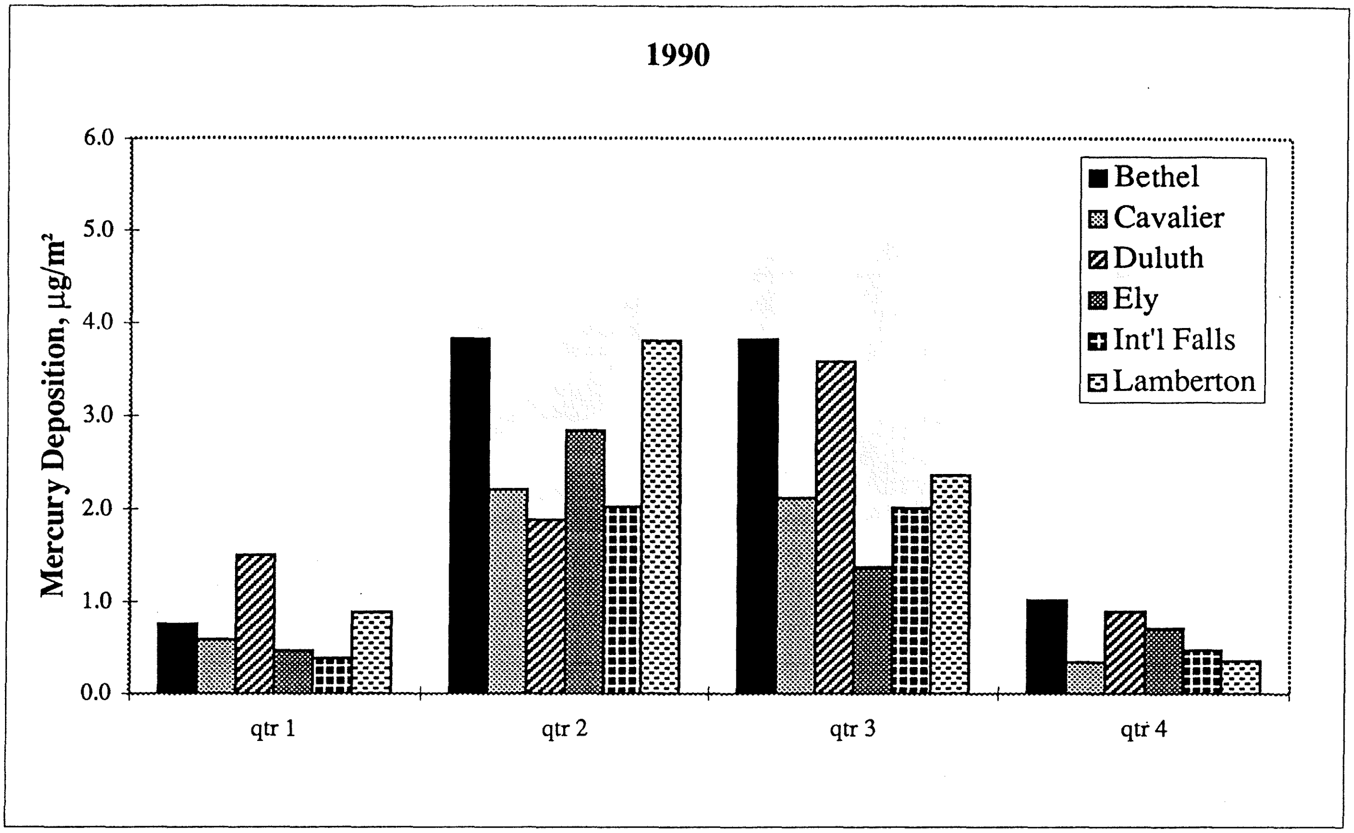


Figure 1.2. Wet mercury deposition as a function precipitation depth for six monitoring sites from 1990 through 1995.



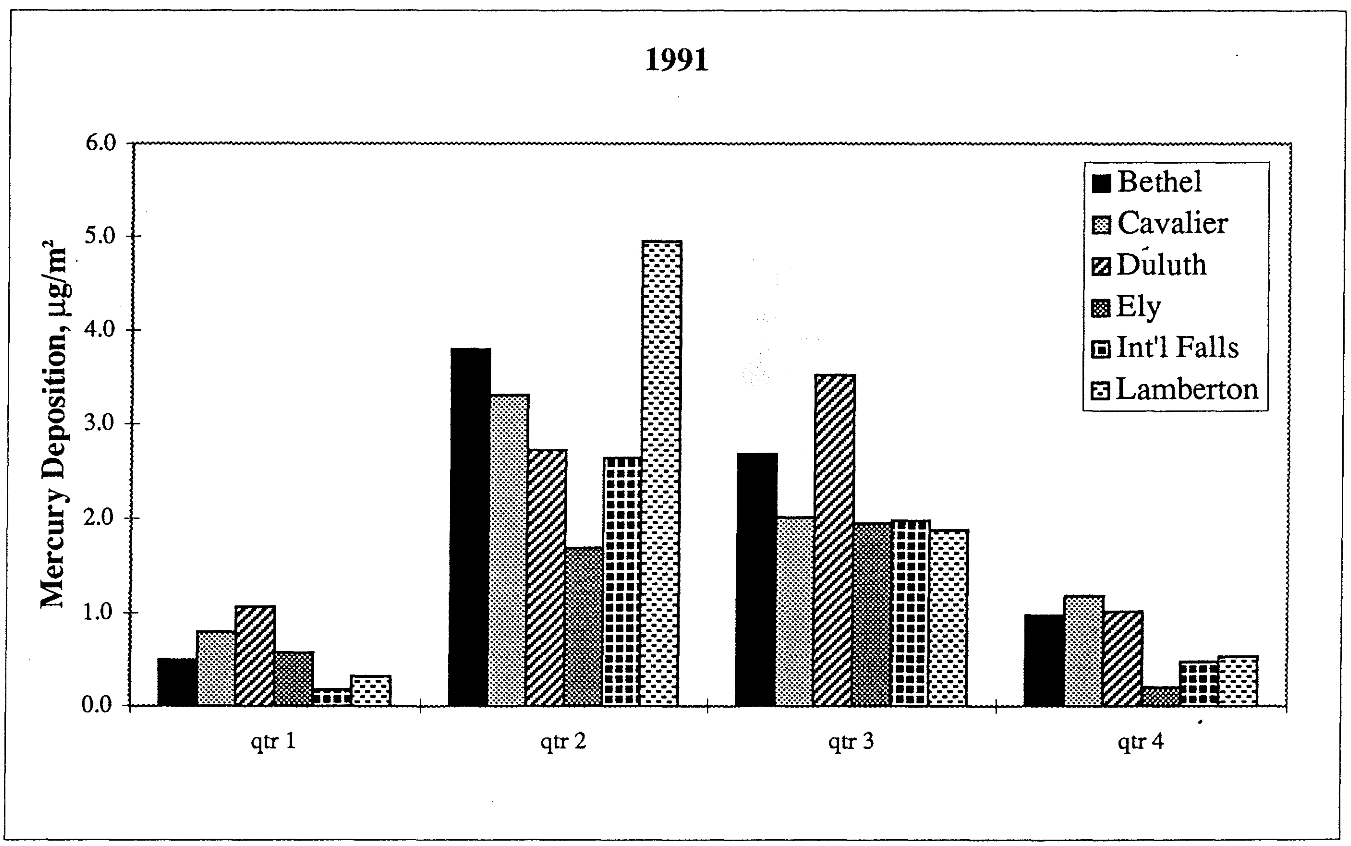
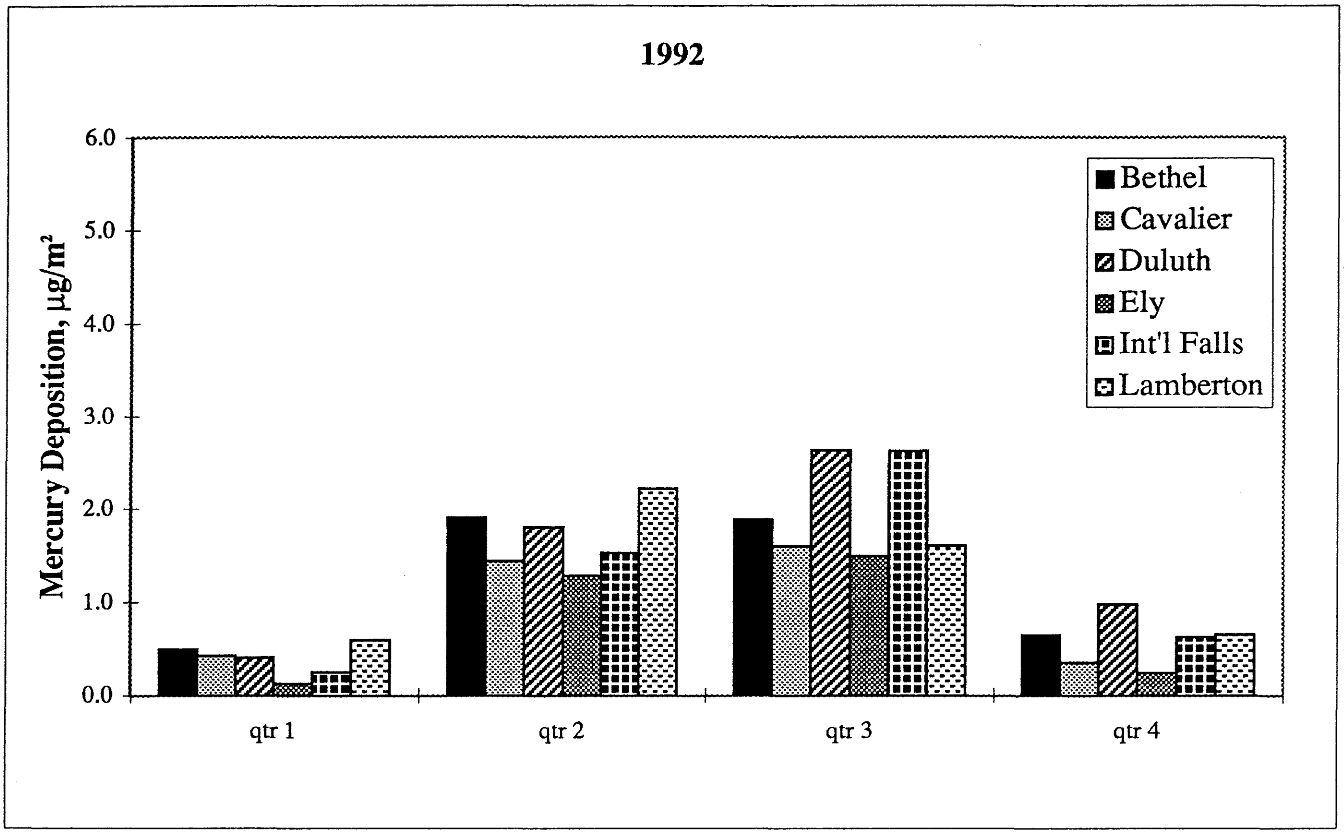
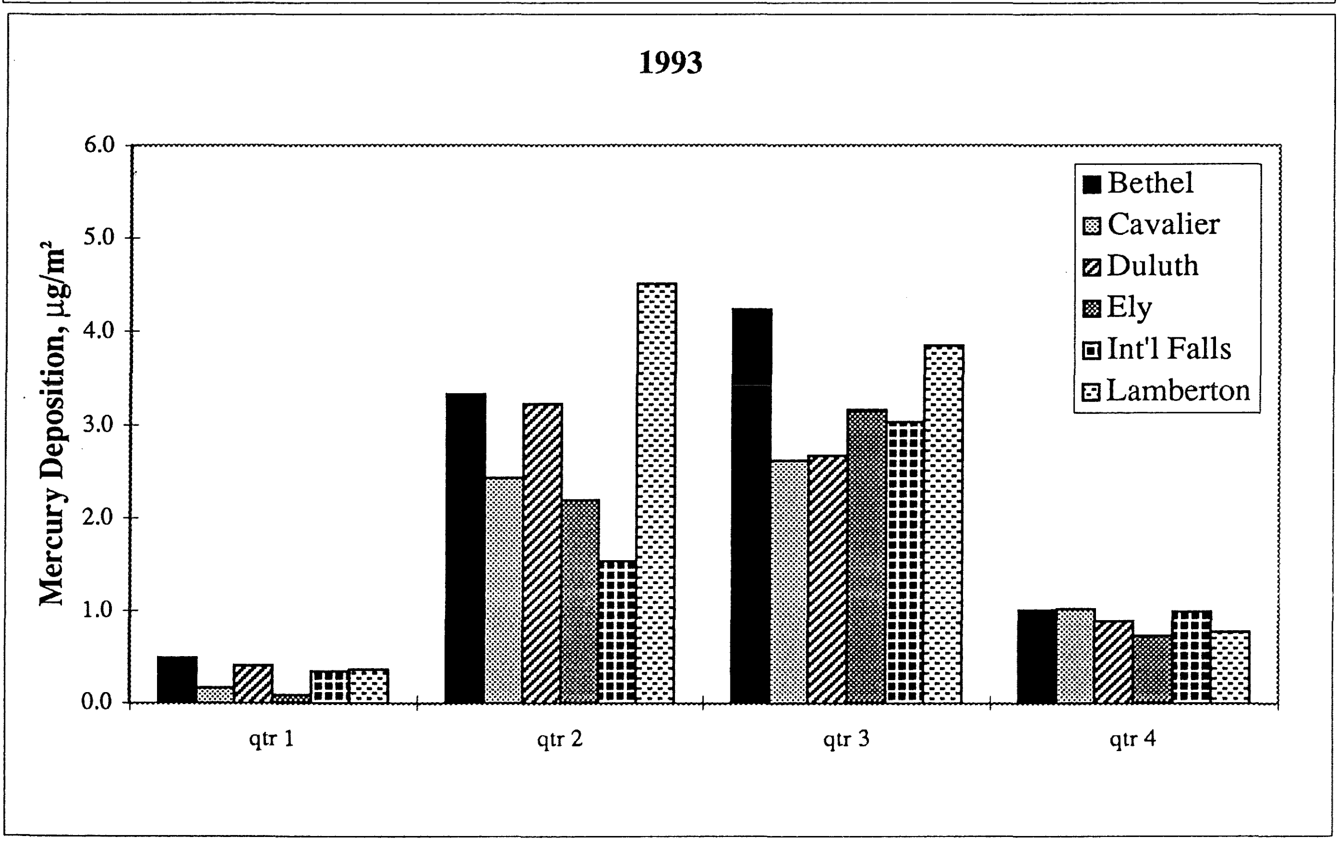
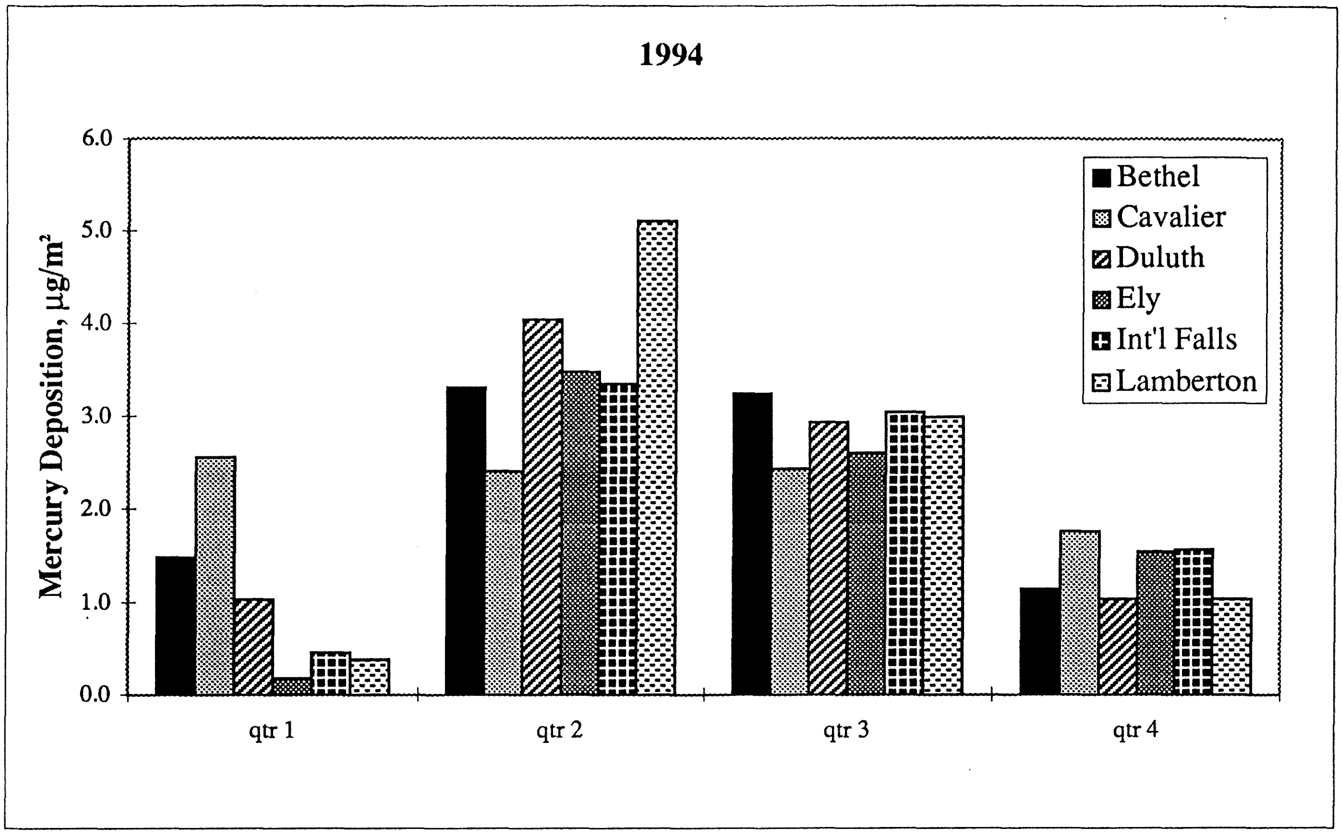
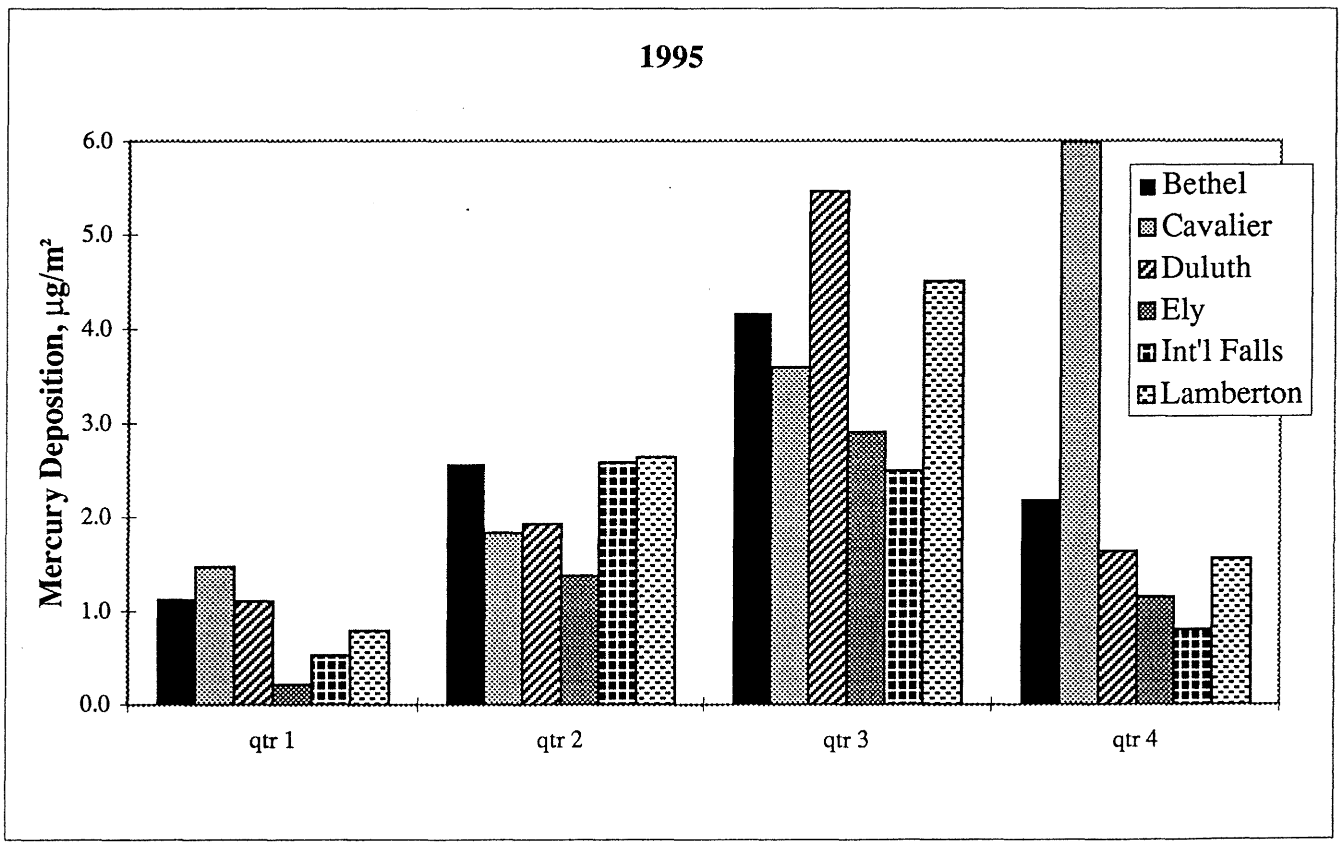


Figure 1.3. Quarterly totals of wet mercury deposition for each of the six long-term monitoring sites from 1990 through 1995.


1992
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Mercury Deposition, µg/m²
Bethel
Cavalier
Duluth
Ely
Int'l Falls
Lamberton
qtr 1
qtr 2
qtr 3
qtr 4


1993
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Mercury Deposition, µg/m²
Bethel
Cavalier
Duluth
Ely
Int'l Falls
Lamberton
qtr 1
qtr 2
qtr 3
qtr 4


1994
Mercury Deposition, µg/m²
6.0
5.0
4.0
3.0
2.0
1.0
0.0
qtr 1
qtr 2
qtr 3
qtr 4
Bethel
Cavalier
Duluth
Ely
Int'l Falls
Lamberton


1995
Mercury Deposition, µg/m²
6.0
5.0
4.0
3.0
2.0
1.0
0.0
qtr 1
qtr 2
qtr 3
qtr 4
Bethel
Cavalier
Duluth
Ely
Int'l Falls
Lamberton

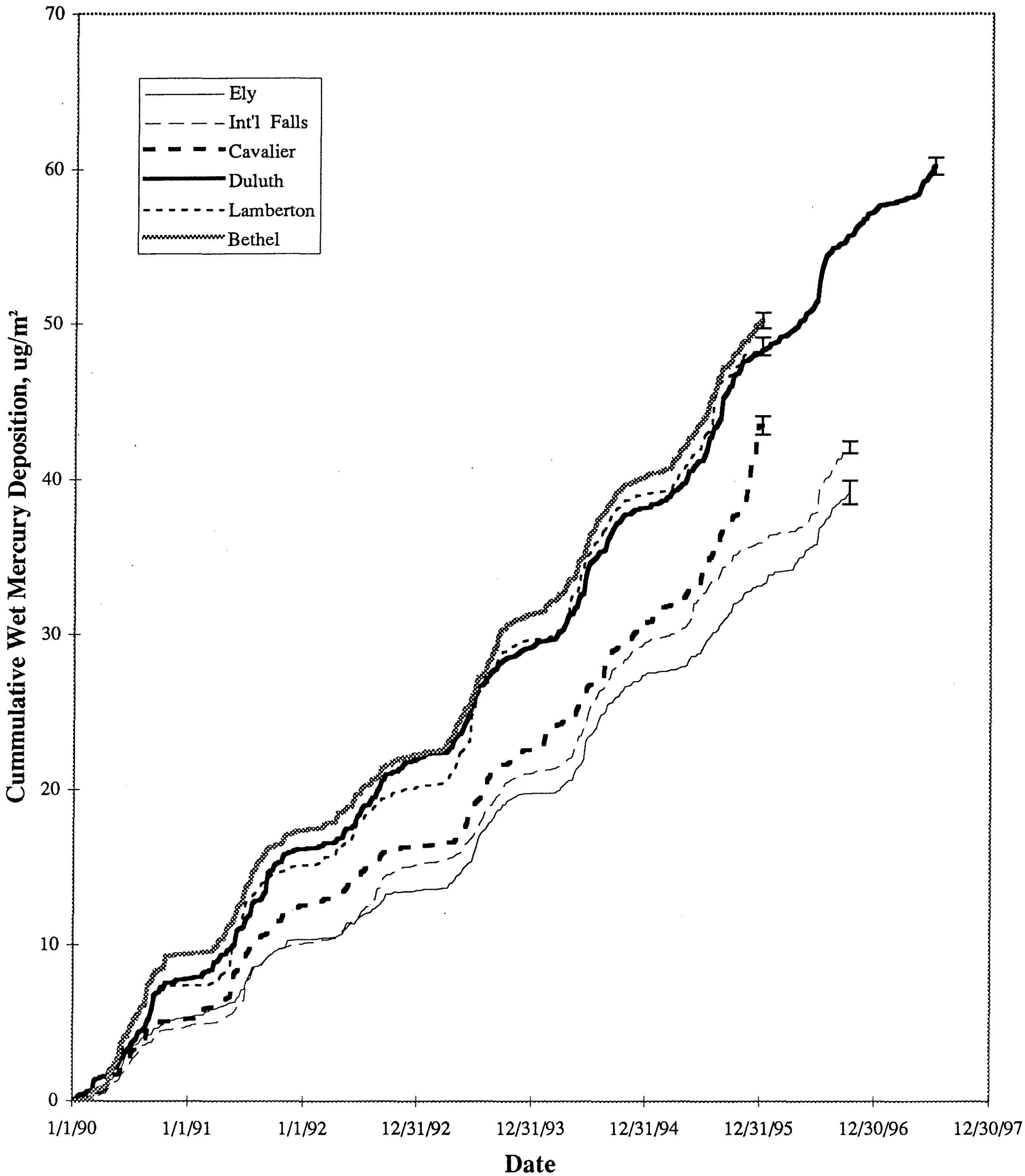


Figure 1.4. Cummulative wet mercury deposition for six long-term monitoring sites starting from January 1, 1990. Error bars represent the estimated standard error of the final value based on the propagation of errors from individual measurements.

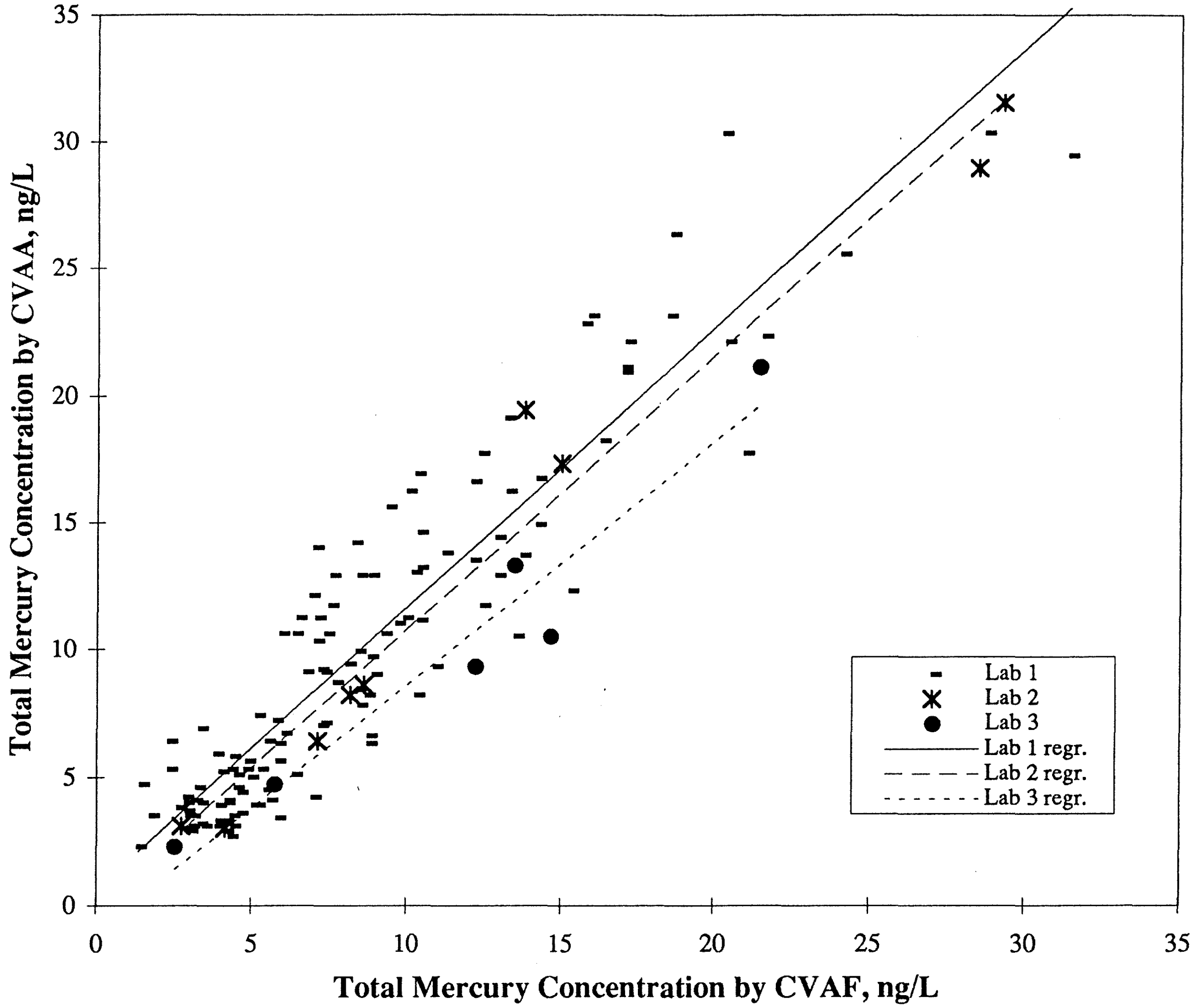


Figure 1.5. Comparison of total mercury concentrations in precipitation and surface water samples as measured using two different digestion and detection techniques. Cold vapor atomic absorption values are from UMD while cold vapor atomic fluorescence values are from 3 independent laboratories. Regression results (CVAA vs CVAF; based on the assumption that CVAA uncertainties are 5x those for CVAF [Sprent and Dolby, 1980]) are as follows:

Lab 1, $y = 1.10 (\pm 0.04) + 0.6 (\pm 0.4)$ $r2 = 0.86$ $n = 125$
Lab 2, $y = 1.08 (\pm 0.07) + 0.0 (\pm 1.2)$ $r2 = 0.97$ $n = 9$
Lab 3, $y = 0.96 (\pm 0.12) - 1.0 (\pm 1.6)$ $r2 = 0.94$ $n = 6$
Lab 1-3, $y = 1.07 (\pm 0.04) + 0.7 (\pm 0.4)$ $r2 = 0.87$ $n = 140$

Tables and Figures for Lake Quality Trends Study..

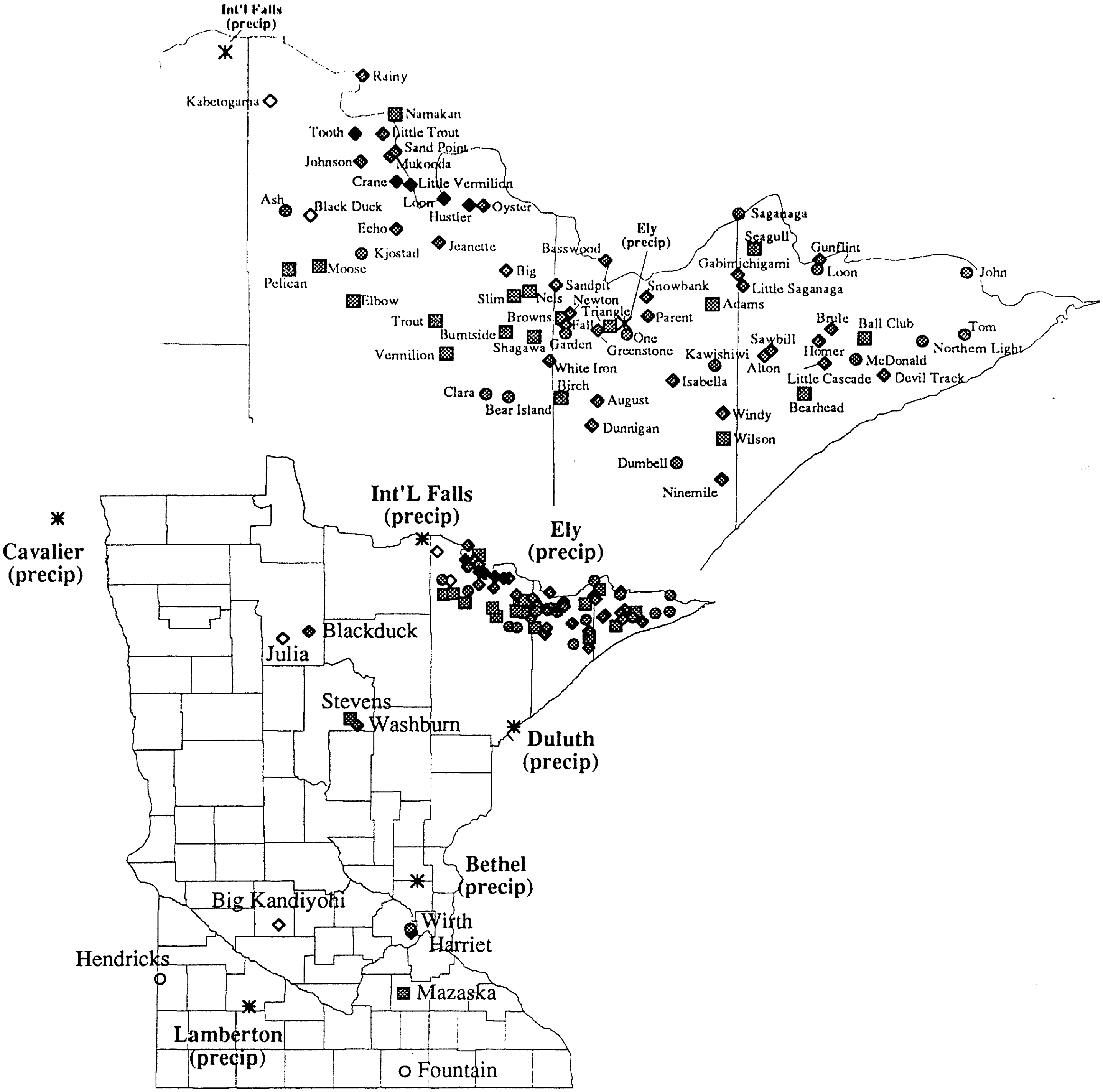


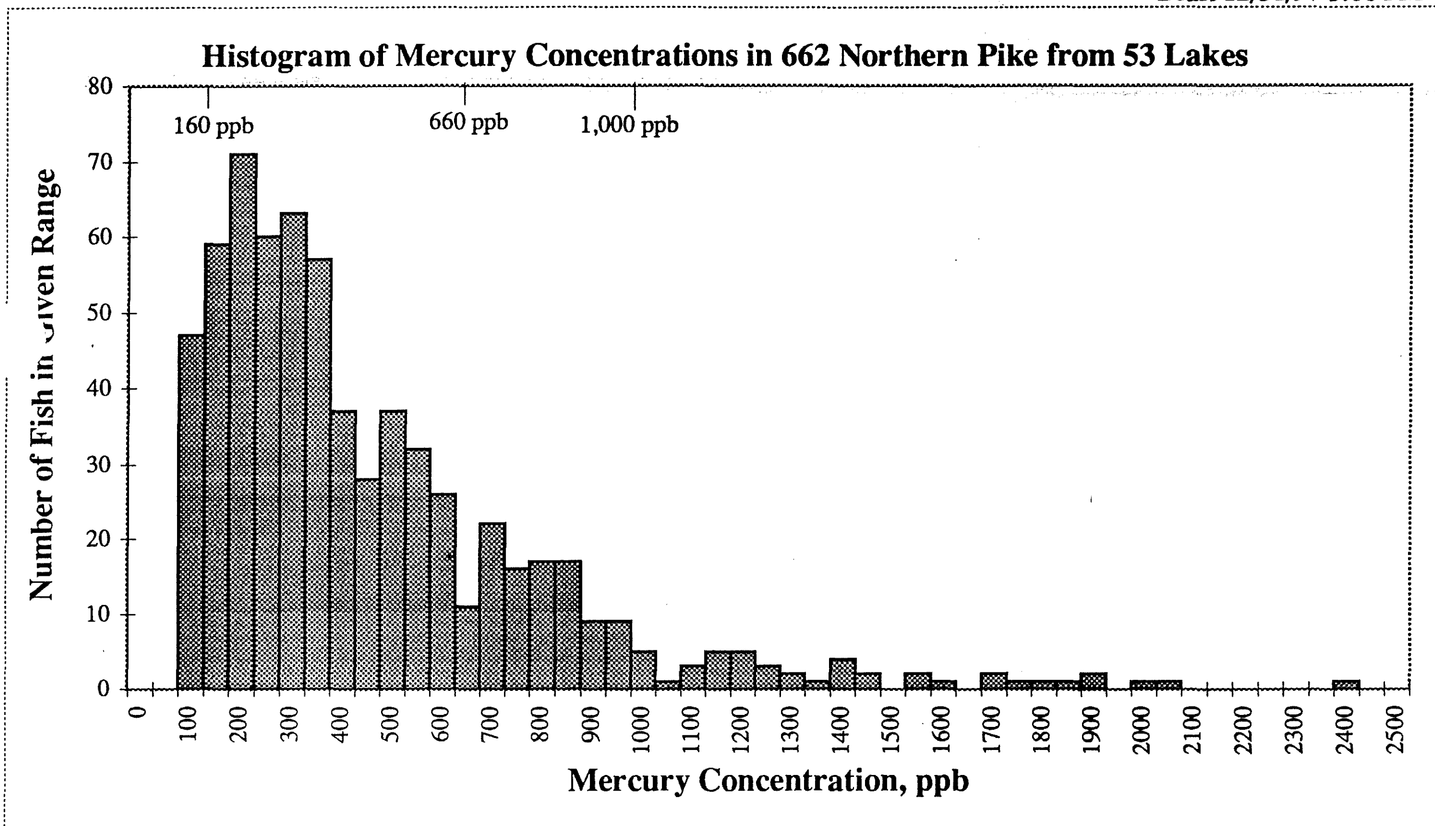
Figure 2.1. Map showing locations of study lakes and long-term precipitation monitoring sites. Precipitation monitoring sites are named for the nearest city or town and designated with an asterisk. Other symbols are for lakes and represent comparison results between historical and recent mercury concentrations in fish (recent relative to historic; fish sizes yielding most significant comparison): diamond - less Hg; square - more Hg; and circle - no significant difference observed. Shading represents recent mercury levels for standard sized fish (northern pike - 55 cm; walleye - 39 cm; shading corresponds to species with highest mercury level) in terms of consumption advisory criteria: no shading - < 160 ppb (no restriction on consumption); gray shading - 160 to 660 ppb (adults: one meal per week month; children: 1 meal per month); and dark shading - ≥ 660 ppb (adults: one meal per month; children: do not eat).

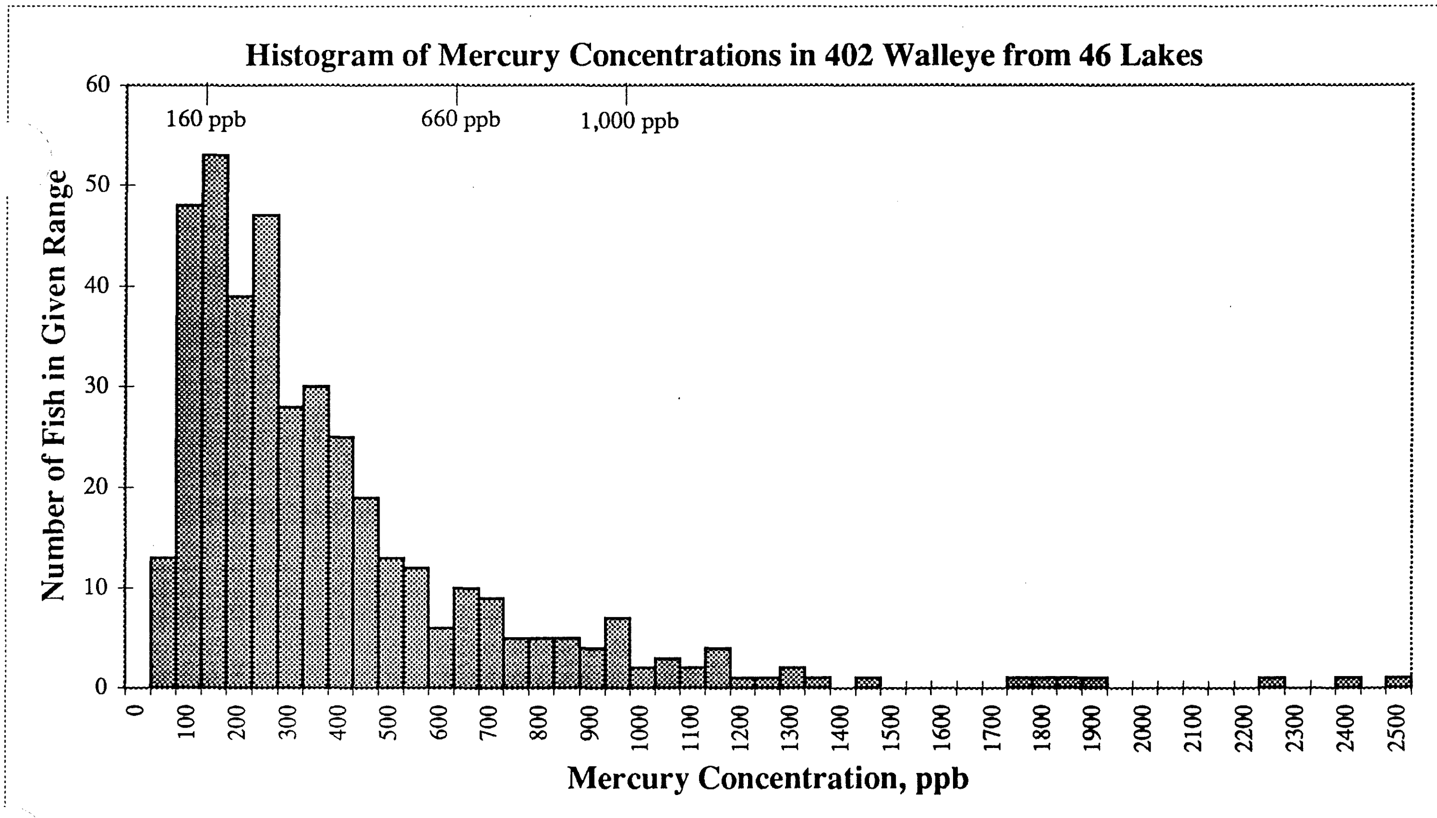
Table 2.1 List of Eighty Study Lakes

Lake Name	County	MNDNR Lake ID	Lake Area (ha)	Hg Conc in 55 cm Nop (ppb)	Hg Diff. Hist. wrt Recent†	Avg. Fish Condition Factor (g/cm^3 * 100)
Adams	Lake	38-0153	198	315	-	0.588
Alton	Cook	16-0622	390	201	0	0.669
Ash	St. Louis	69-0864	278	266	0	0.624
^ugust	Lake	38-0691	77	534	0	0.558
ll Club	Cook	16-0182	82		na	
ꞵasswood	Lake	38-0645	10670	283	+	0.580
Bear Head	St. Louis	69-0254	265	289	na	0.502
Bear Island	St. Louis	69-0115	915	478	0	0.565
Big	St. Louis	69-0190	762	227	+	0.534
Big Kandiohi	Kandiyohi	34-0086	1200 (est)		na	
Birch	St. Louis	69-0003	2500	415	-	0.632
Black Duck	St. Louis	69-0842	499		na	
Blackduck	Beltrami	04-0069	1110	182	+	0.516
Browns	Lake	38-0780	85	222	-	0.579
Brule	Cook	16-0348	2106		na	
Burntside	St. Louis	69-0118	2950	401	-	0.629
Clara	Cook	16-0365	158		na	
Crane	St. Louis	69-0616	1196	614	+	0.610
Devil Track	Cook	16-0143	744		na	
Dumbell	Lake	38-0393	193		na	
Dunnigan	Lake	38-0664	33		na	
Echo	St. Louis	69-0615	455	220	+	0.570
Elbow	St. Louis	69-0744	687	440	-	0.600
l	Lake	38-0811	885	304	+	0.588
.untain	Freeborn	24-0018	225		na	
Gabimichigami	Cook	16-0811	483	224	+	0.629
Garden	Lake	38-0738	254	391	0	0.636
Greenstone	Lake	38-0718	134	231	+	0.583
Gunflint	Cook	16-0356	1637	227	+	0.580
Harriet	Hennepin	27-0016	136	222	na	0.675
Hendricks	Lincoln	41-0110	661	130	na	0.538
Homer	Cook	16-0406	177	230	+	0.559
Hustler	St. Louis	69-0343	109	734	+	0.564
Isabella	Lake	38-0396	516	384	+	0.572
Jeanette	St. Louis	69-0456	241	345	+	0.561
John	Cook	16-0035	76	268	0	0.568
Johnson	St. Louis	69-0691	684	264	+	0.613
Julia	Beltrami	04-0166	199	131	+	0.606
Kabetogama	St. Louis	69-0845	10425	141	+	0.581
Kawishiwi	Lake	38-0080	158	212	na	0.535
Kjostad	St. Louis	69-0748	179	544	0	0.586
Little Cascade	Cook	16-0347	107	470	+	0.590
Little Saganaga	Cook	16-0809	669	263	+	0.584
'le Trout	St. Louis	69-0682	105		na	
.ttle Vermilion	St. Louis	69-0608	431	598	0	0.558
Loon	St. Louis	69-0470	947	676	+	0.549
Loon	Cook	16-0448	452	234	0	0.704
Mazaska	Rice	66-0039	278	181	na	0.610
McDonald	Cook	16-0235	35	229	na	0.543

Lake Name	County	MNDNR Lake ID	Lake Area (ha)	Hg Conc in 55 cm Nop (ppb)	Hg Diff. Hist. wrt Recent†	Avg. Fish Condition Factor (g/cm^3 * 100)
Moose	St. Louis	69-0806	373	427	-	0.574
Mukooda	St. Louis	69-0684	314	173	na	0.654
Namakan	St. Louis	69-0693	5686	303	+	0.625
Nels	St. Louis	69-0080	71		na	
Newton	Lake	38-0784	210	529	+	0.530
Ninemile	Lake	38-0033	121		na	
Northern Light	Cook	16-0089	135	268	0	0.578
One	Lake	38-0605	289	369	na	0.572
Oyster	St. Louis	69-0330	311	514	+	0.535
Parent	Lake	38-0526	180		na	
Pelican	St. Louis	69-0841	4663	352	-	0.546
Rainy	St. Louis	69-0694	89357	276	+	0.561
Saganaga	Cook	16-0633	7374	392	0	0.596
Sand Point	St. Louis	69-0617	3419	405	+	0.617
Sandpit	Lake	38-0786	24	640	+	0.610
Sawbill	Cook	16-0496	340	175	+	0.627
Seagull	Cook	16-0629	1626	463	-	0.543
Shagawa	St. Louis	69-0069	941		na	
Slim	St. Louis	69-0181	126		na	
Snowbank	Lake	38-0529	1860	199	+	0.553
Stevens	Cass	11-0116	57	582	-	0.612
Tom	Cook	16-0019	165		na	
[illegible]oth	St. Louis	69-0756	24	1846	+	0.408
Triangle	Lake	38-0715	122	336	-	0.574
Trout	St. Louis	69-0498	3309	279	-	0.633
Vermilion	St. Louis	69-0378	12384	250	-	0.574
Washburn	Cass	11-0059	715	239	+	0.604
White Iron	St. Louis	69-0004	1278	447	+	0.630
Wilson	Lake	38-0047	260		na	
Windy	Lake	38-0068	184	571	+	0.608
Wirth	Hennepin	27-0037	15	142	na	0.610

†Negative and positive differences (P > 0.9) are designated "-" and "+", respectively. No significant difference is designated "0". Insufficent data for comparison is marked "na".





gure 2.2. Histograms of mercury concentrations in northern pike and walleye from 80 Minnesota lakes sampled in 1995 and 1996. Health consumption advisories are: 0-160 ppb - unlimited meals for adults and children; 160-660 ppb - one meal per week for adults, one meal per month for children ages 0-6 and child bearing women; 660-2800 ppb - one meal per month for adults, do not eat for children and child bearing women; and > 1000 ppb - FDA restriction limit for interstate shipment.

Table 2.2. Summary of Comparisons Between Historical and Recent Mercury in Fish Data for Fish Length Ranges Yielding the Maximum Statistical Significance.

		Northern Pike							Walleye						
Lake	Lake	Collection Yr		Highest	Length Range		Difference[b]		Collection Yr		Highest	Length Range		Difference[b]	
Name	ID	Hist	Recent	Signif[a]	Low	High	ng/g	%	Hist	Recent	Signif[a]	Low	High	ng/g	%
Adams	38-0153	82	96	*	72.3	76.2	-175	-38			na				
Alton	16-0622	86	96	ns	42.4	73.2	23	10	86	96	**	42.7	51.4	121	37
Ash	69-0864	83	95	ns	47.0	71.8	-20	-7			na				
August	38-0691	92	96	ns	44.5	51.4	108	22	92	96		46.0	48.3	241	34
Ball Club	16-0182			na					82	95	*	46.7	51.7	-531	-209
Basswood	38-0645	77	96	**	44.8	60.5	205	45			na				
Bear Head	69-0254	83	95	†					83	95	†				
Bear Island	69-0115	83	96	ns	72.0	85.0	30	3			na				
Big	69-0190	82	96	*	43.4	65.9	117	34	82	96	*	31.2	35.6	173	53
Big Kandiohi	34-0086			na					91	96	**	35.1	46.9	49	37
Birch	69-0003	76	96	**	46.9	63.6	-124	-42			na				
Black Duck	69-0842			na					82	95	**	44.9	47.6	151	52
Blackduck	04-0069	86	96	*	49.0	50.5	42	22	86	96		37.3	52.3	48	32
Browns	38-0780	91	96		37.4	58.1	-38	-29	91	96	*	32.3	38.2	-54	-80
Brule	16-0348			na					86	96	**	31.5	52.8	362	60
Burntside	69-0118	77	95	**	56.9	69.9	-104	-27	77	95	**	28.4	43.9	-157	-54
Clara	16-0365			na					91	96	*	33.0	36.8	-87	-70
Crane	69-0616	76	95/96	**	48.0	78.0	340	30	76	96	**	39.2	49.8	454	32
Devil Track	16-0143			na					90	96	*	42.4	50.6	164	35
Dumbell	38-0393			na					83	96	ns	31.5	56.9	46	15
Dunnigan	38-0664			na					87	96	*	40.6	50.3	340	35
Echo	69-0615	91	96	**	45.7	69.6	281	55	91	96		35.6	52.8	555	65
Elbow	69-0744	83	95		56.3	68.2	-101	-24	92	95	ns	35.6	51.3	84	16
Fall	38-0811	77	95	**	54.9	65.2	196	39	77	95	**	23.6	36.8	118	38
Fountain	24-0018			na					91	96	†				
Gabimichigami	16-0811	82	95	*	47.7	62.9	105	32			na				
Garden	38-0738	83	96	ns	47.2	103.4	24	4			na				
Greenstone	38-0718	92	96	**	53.7	76.2	176	34	92	96	ns	36.1	53.6	-81	-32
Gunflint	16-0356	77	96	**	38.9	55.1	79	34	77	96	**	38.4	53.1	163	30
Harriet	27-0016		96	†					89	96	**	48.1	56.4	575	44
Hendricks	41-0110		96	†					91	96	ns	27.2	52.2	99	45
Homer	16-0406	93	96	*	54.3	58.3	72	23			na				
Hustler	69-0343	84	96	**	48.6	58.0	276	29			na				
Isabella	38-0396	83	96	*	48.1	70.4	185	31			na				
Jeanette	69-0456	86	96	**	50.7	57.7	334	50	86	96	*	30.5	34.7	108	31
John	16-0035	91	96	ns	55.9	85.1	-68	-18			na				
Johnson	69-0691	84	96	*	43.9	60.4	127	36			na				
Julia	04-0166	86	96	**	48.0	65.5	233	62	86	96	**	35.6	53.8	167	52
Kabetogama	69-0845	86	95/96	**	50.5	68.0	232	57	86	96	**	32	60.5	516	73
Kawishiwi	38-0080	83	96	†					83	96	†				
Kjostad	69-0748	82	96	ns	47.5	69.9	173	21			na				
Little Cascade	16-0347	82	96	*	49.9	65.7	170	25			na				
Little Saganaga	16-0809	87	95	**	51.6	78.0	263	45			na				
Little Trout	69-0682			na					91	95		46.7	58.2	167	28
Little Vermilion	69-0608	91	96	ns	55.9	83.1	202	17	91	96	*	49.9	63.5	245	15
Loon	69-0470	82	96	*	45.4	61.8	164	20			nd				
Loon	16-0448	85	96	ns	64.0	78.4	63	9			nd				
Mazaska	66-0039		96	†					92	96		56.3	63.1	-116	-37

		Northern Pike							Walleye						
Lake	Lake	Collection Yr		Highest	Length Range		Difference[b]		Collection Yr		Highest	Length Range		Difference[b]	
Name	ID	Hist	Recent	Signif[a]	Low	High	ng/g	%	Hist	Recent	Signif[a]	Low	High	ng/g	%
McDonald	16-0235	82	96	†						96	†				
Moose	69-0806	93	96		47.2	55.5	-96	-32			nd				
Mukooda	69-0684		95	†					87	95	*	50.0	53.8	163	26
Namakan	69-0693	90	95/96	**	55.6	65.2	128	24	77	96	**	41.5	44.5	-232	-111
[illegible]ls	69-0080			nd					91	96	*	51.9	55.1	-163	-18
[illegible]vton	38-0784	91	95		69.2	80.0	244	24			nd				
Ninemile	38-0033			nd					91	95	**	52.4	53.6	300	35
Northern Light	16-0089	82	95	ns	43.2	70.4	-40	-17			nd				
One	38-0605	84	96	†					84	96	†				
Oyster	69-0330	82	96	**	43.4	63.1	362	44			nd				
Parent	38-0526			nd					82	96	*	49.3	55.4	121	21
Pelican	69-0841	77	95	**	58.8	64.4	-94	-28	77	95	ns	46.2	50.6	-21	-5
Rainy	69-0694	76	95/96	**	49.8	74.7	296	44	90	96		44.3	56.1	394	52
Saganaga	16-0633	85	95	ns	45.5	70.6	189	30	82	95	ns	32.5	52.2	69	18
Sand Point	69-0617	90	95/96	**	55.1	83.6	292	28	77	96	*	52.8	53.3	931	44
Sandpit	38-0786	84	96	*	64.9	66.0	734	48			nd				
Sawbill	16-0496	82	96	**	46.0	55.8	179	53	82	96	†				
Seagull	16-0629	83	96	**	62.5	81.6	-697	-219	91	96	ns	35.8	68.2	130	23
Shagawa	69-0069			nd					83	95	**	34.5	43.3	-87	-77
Slim	69-0181			nd					82	96	*	31.8	39.2	-74	-23
Snowbank	38-0529	83	96	**	59.6	61.5	158	42			nd				
Stevens	11-0116	82	96	*	45.2	66.3	-150	-34			nd				
Tom	16-0019			nd					90	96	ns	29.7	41.3	-13	-6
Tooth	69-0756	87	95		42.4	43.9	194	21			nd				
[illegible]ngle	38-0715	91	96		59.7	72.5	-93	-23	91	96	*	56.3	60.7	-389	-112
[illegible]out	69-0498	92	96	**	57.9	73.5	-128	-55			nd				
Vermilion	69-0378	77	95	**	56.1	83.8	-176	-80	77	95		40.8	46.6	-50	-25
Washburn	11-0059	85	96	*	43.2	63.4	108	32			nd				
White Iron	69-0004	82	96	**	50.1	56.8	193	31	77	96	*	28.6	38.3	83	21
Wilson	38-0047			nd					93	96	**	29	33.4	-41	-44
Windy	38-0068	82	95	*	56.0	81.0	122	14			nd				
Wirth	27-0037	90	96	†					90	96	ns	40.8	43.6	-17	-12

[a]Symbols represent statistical significance levels for one-tailed t-tests:
** - ≥ 99%; * - ≥ 95% & < 99%; blank - ≥ 90% & < 95%; ns - <90%; † - n ≤ 2 for historical data; and na - no data.

[b]Differences are with respect to recent data.

			Mercury Concentration Difference							
			Absolute, ng/g				%			
Species	difference	n	mean	sd	range		mean	sd	range	
	significant neg.	12	-165	172	-697	-38	-53	55	-219	-23
N. Pike	non-significant	11	62	94	-68	202	144	16	-18	30
	significant pos.	31	213	127	42	734	36	12	14	62
	significant neg.	12	-165	151	-531	-41	-72	54	-209	-18
Walleye	non-significant	9	33	69	-81	130	19.1	23	-32	45
	significant pos.	25	268	208	48	931	39	14	15	73
	significant neg.	19								
Walleye	non-significant	13								
or	significant pos.	43								
N. Pike	conflicting	1								
	insuf. hist. data	4								

Key For Figure Explanation

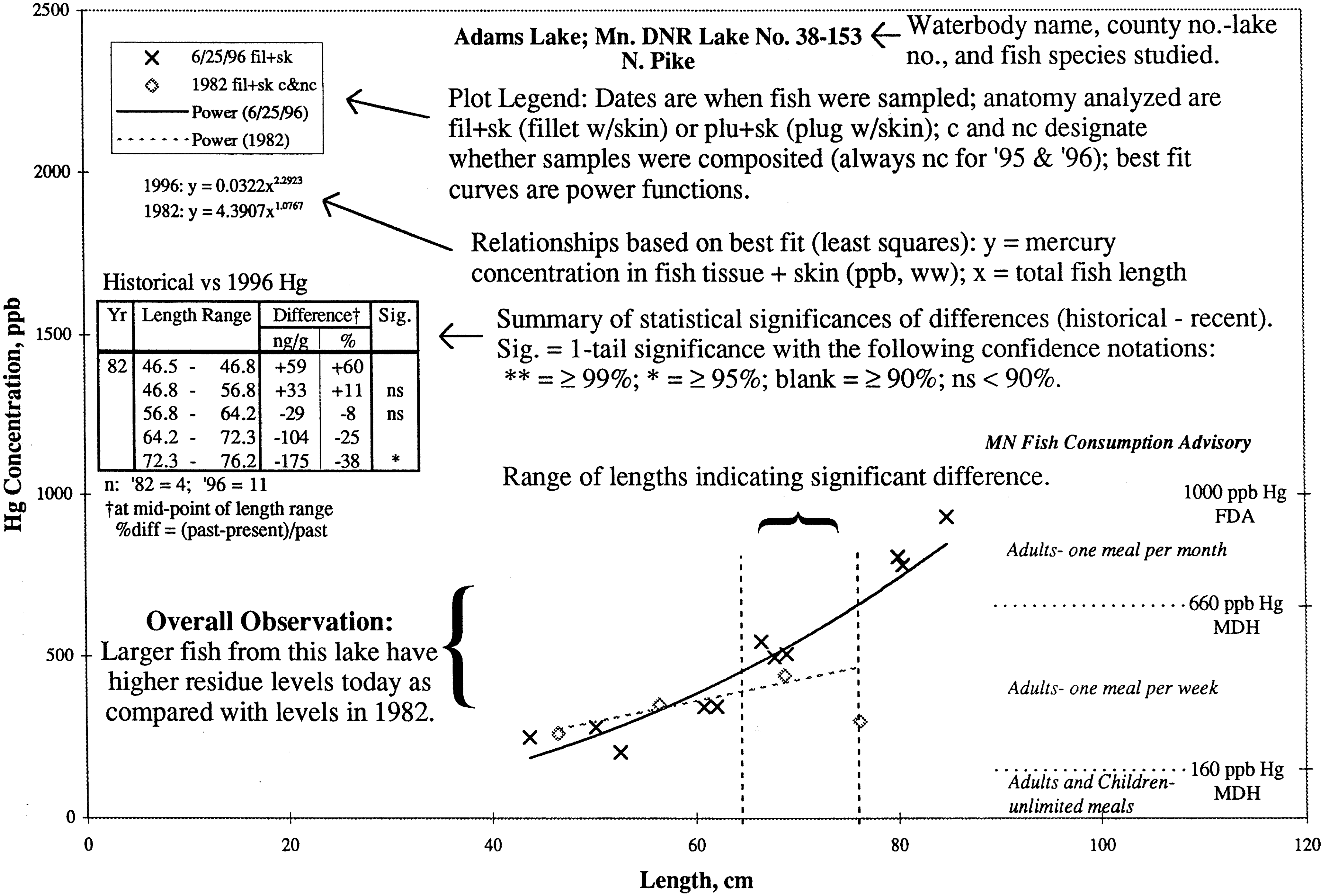
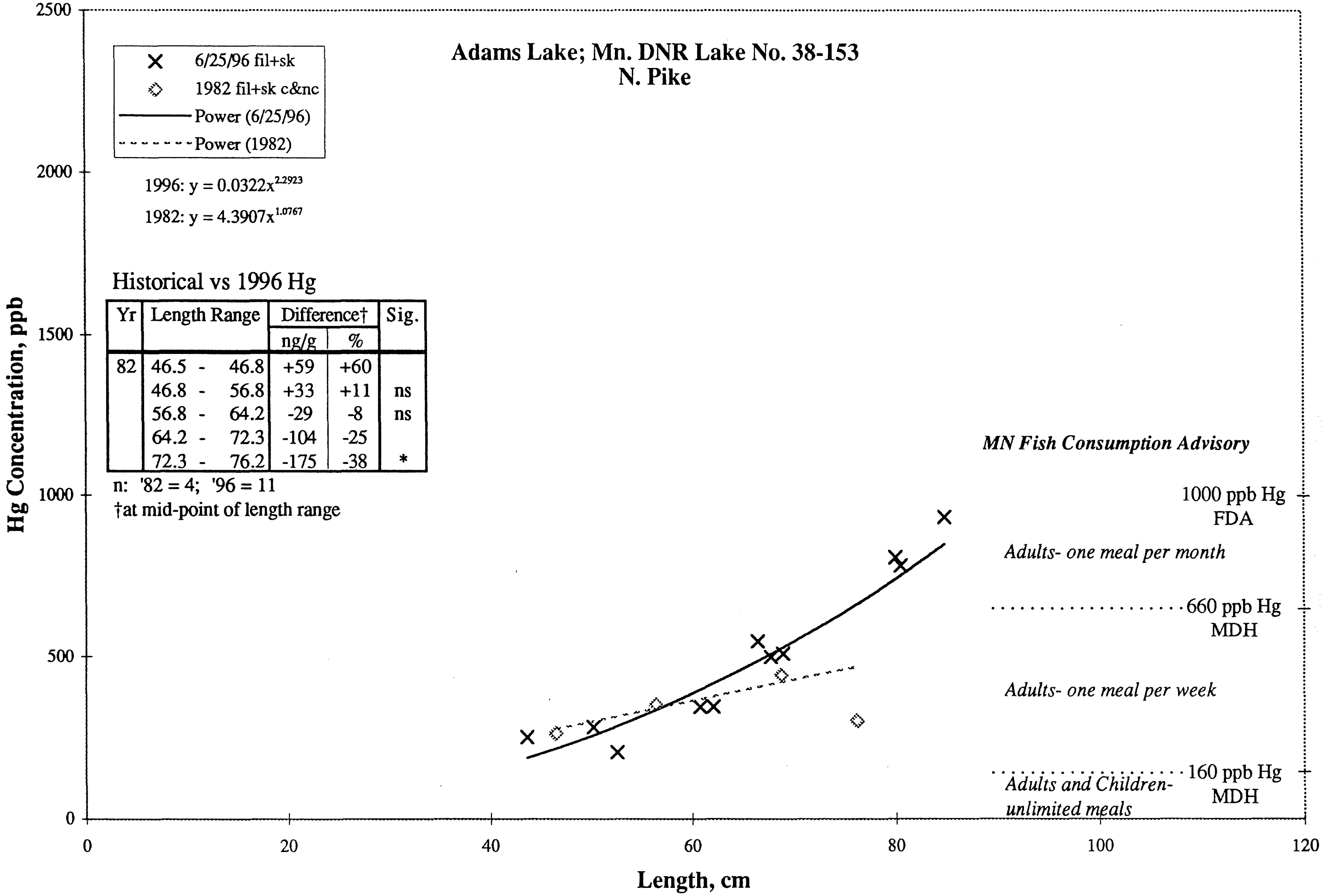


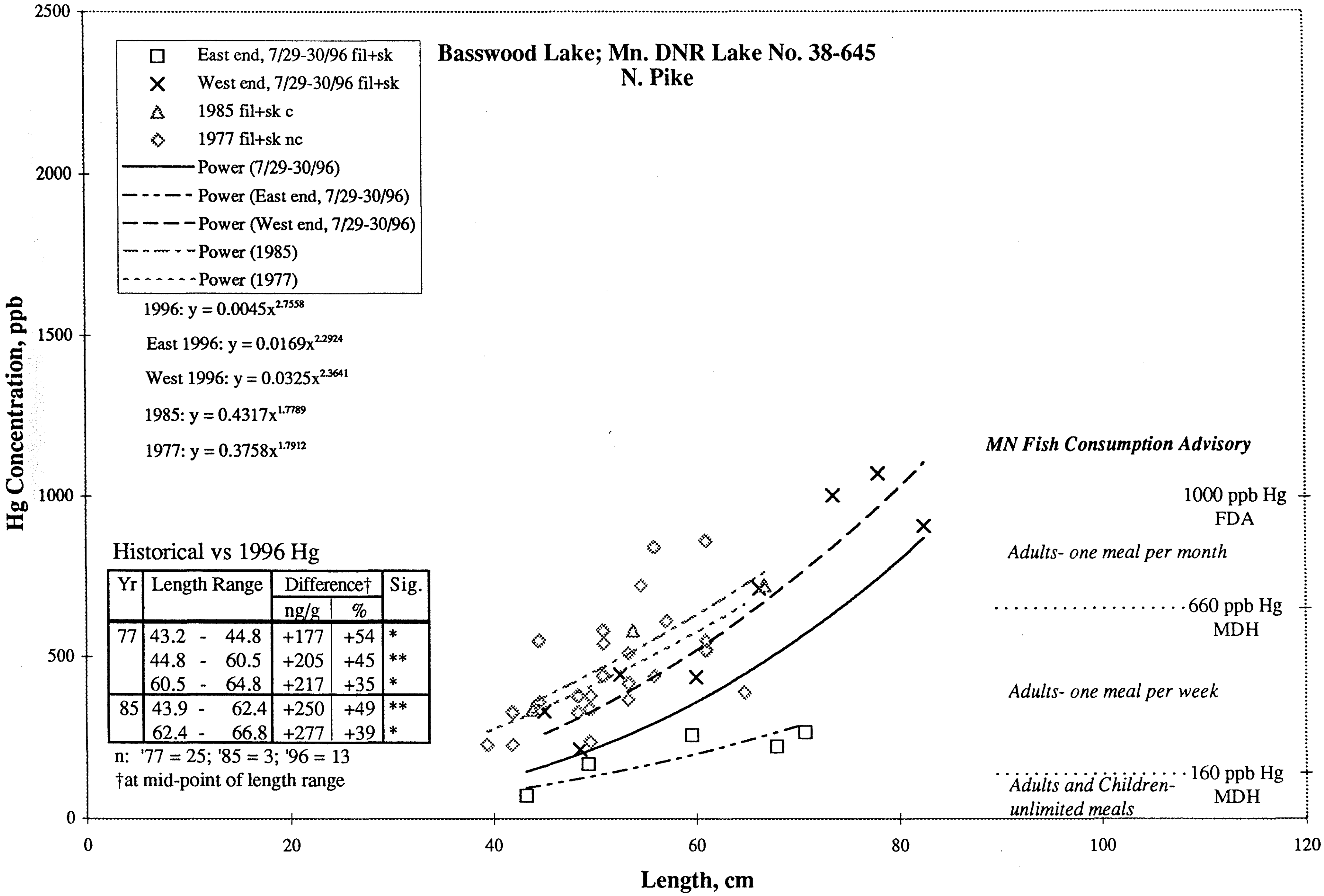
Figure 2.3. Plots of fish fillet mercury residue levels (ww) vs fish length.



Historical vs 1996 Hg

Yr	Length Range	Difference† ng/g	Difference† %	Sig.
82	46.5 - 46.8	+59	+60	
	46.8 - 56.8	+33	+11	ns
	56.8 - 64.2	-29	-8	ns
	64.2 - 72.3	-104	-25	
	72.3 - 76.2	-175	-38	*

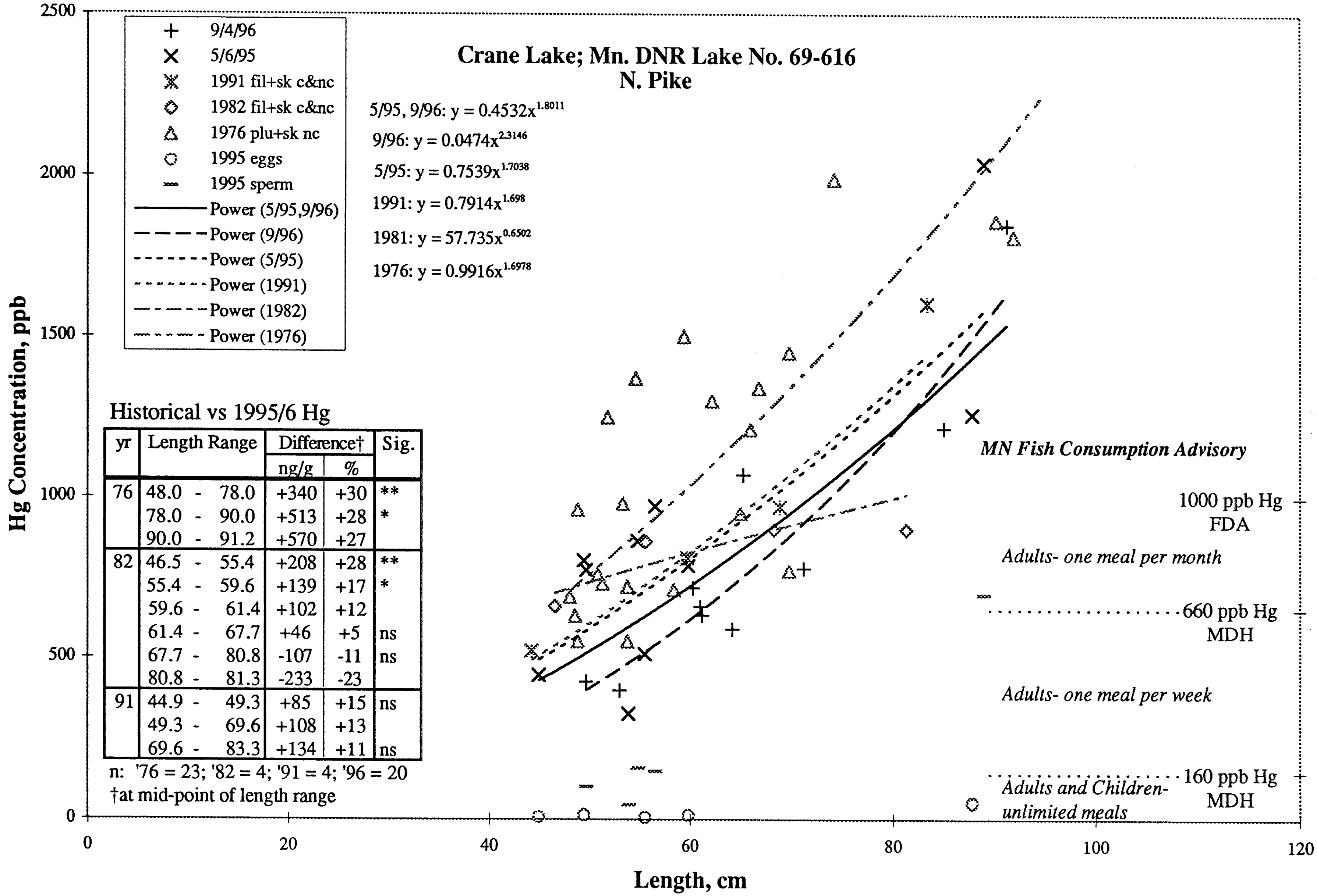
n: '82 = 4; '96 = 11
†at mid-point of length range



Historical vs 1996 Hg

Yr	Length Range	Difference† ng/g	Difference† %	Sig.
77	43.2 - 44.8	+177	+54	*
	44.8 - 60.5	+205	+45	**
	60.5 - 64.8	+217	+35	*
85	43.9 - 62.4	+250	+49	**
	62.4 - 66.8	+277	+39	*

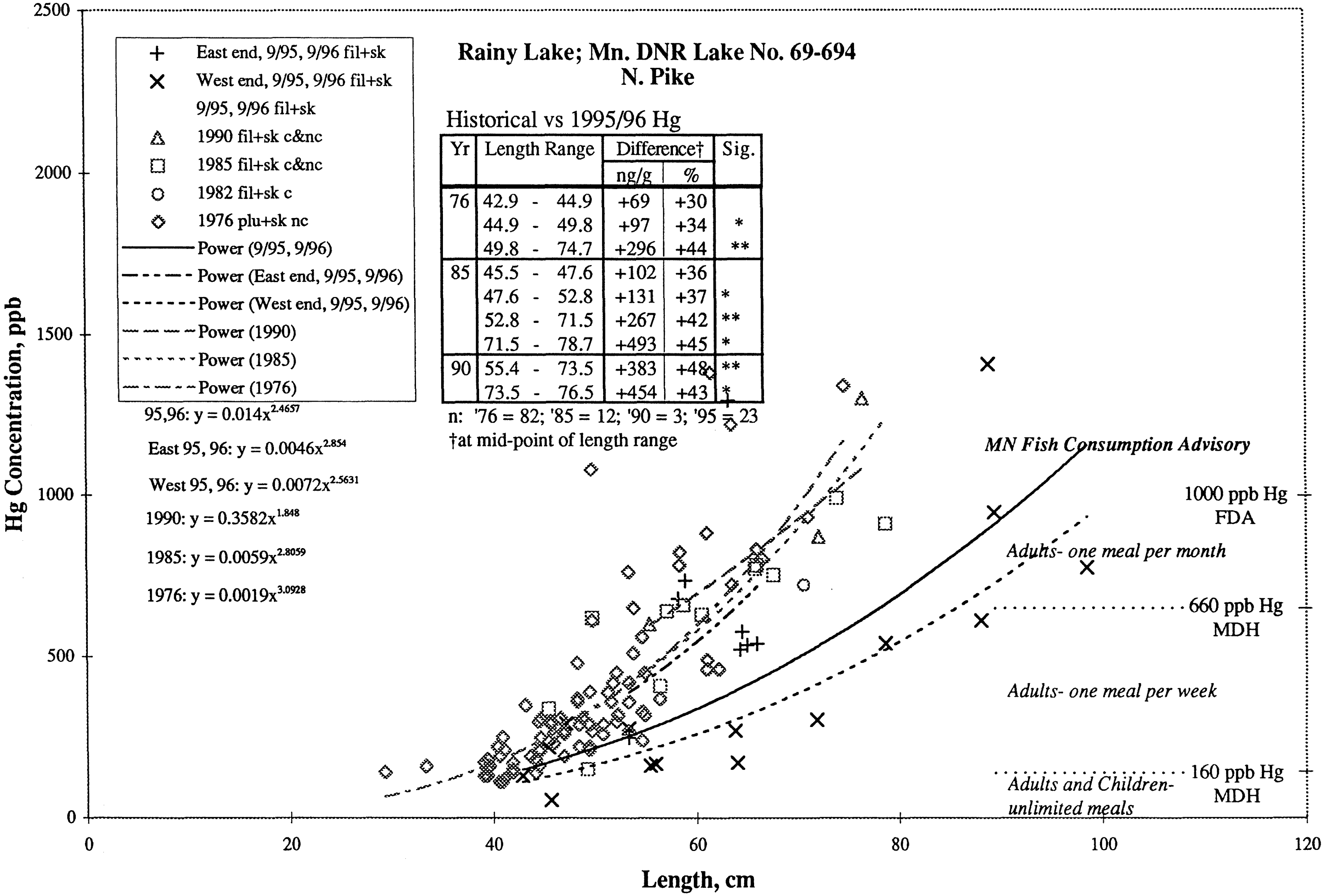
n: '77 = 25; '85 = 3; '96 = 13
†at mid-point of length range



Historical vs 1995/6 Hg

yr	Length Range	Difference† ng/g	Difference† %	Sig.
76	48.0 - 78.0	+340	+30	**
	78.0 - 90.0	+513	+28	*
	90.0 - 91.2	+570	+27	
82	46.5 - 55.4	+208	+28	**
	55.4 - 59.6	+139	+17	*
	59.6 - 61.4	+102	+12	
	61.4 - 67.7	+46	+5	ns
	67.7 - 80.8	-107	-11	ns
	80.8 - 81.3	-233	-23	
91	44.9 - 49.3	+85	+15	ns
	49.3 - 69.6	+108	+13	
	69.6 - 83.3	+134	+11	ns

n: '76 = 23; '82 = 4; '91 = 4; '96 = 20
†at mid-point of length range

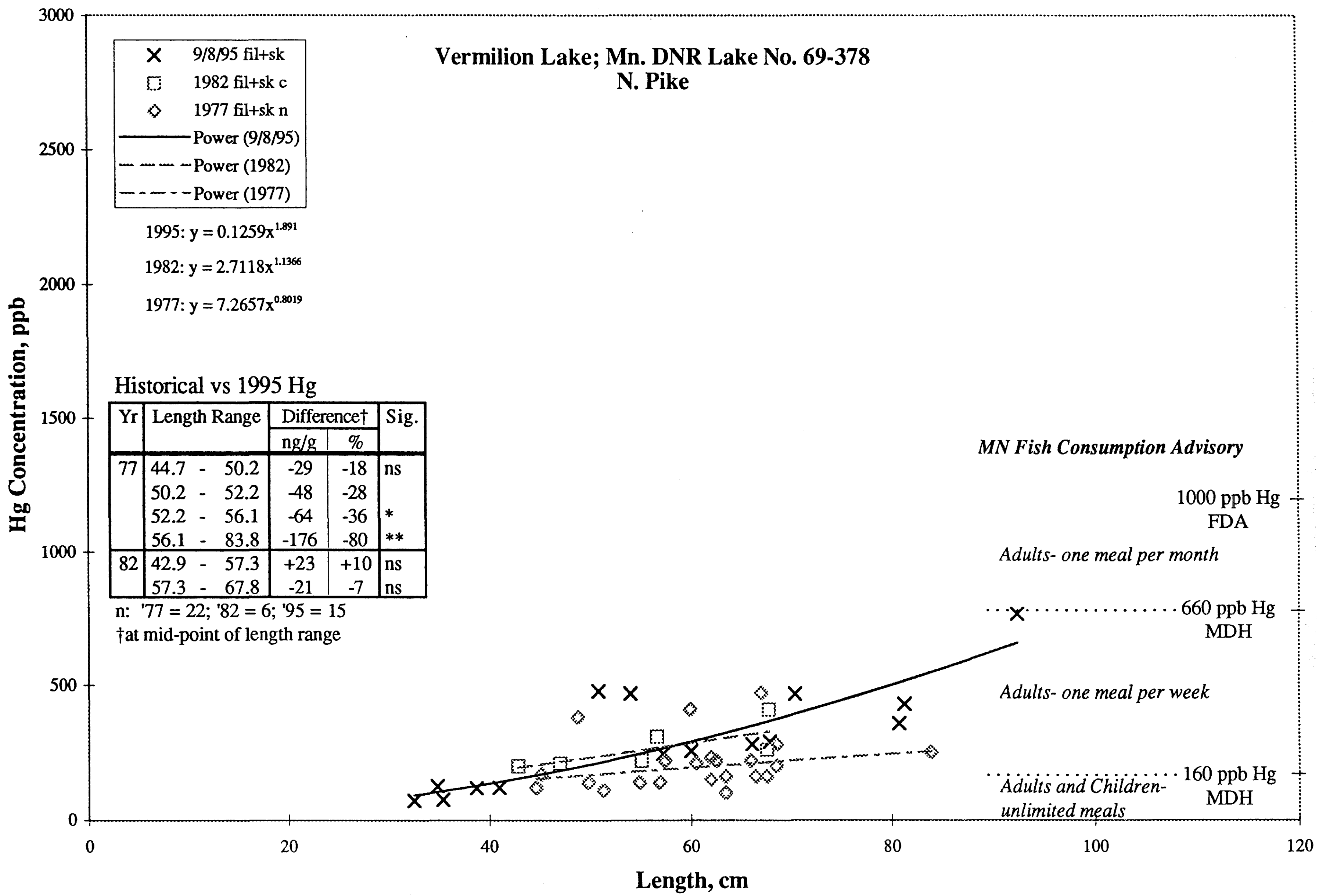


Historical vs 1995/96 Hg

Yr	Length Range	Difference† ng/g	Difference† %	Sig.
76	42.9 - 44.9	+69	+30	
	44.9 - 49.8	+97	+34	*
	49.8 - 74.7	+296	+44	**
85	45.5 - 47.6	+102	+36	
	47.6 - 52.8	+131	+37	*
	52.8 - 71.5	+267	+42	**
	71.5 - 78.7	+493	+45	*
90	55.4 - 73.5	+383	+48	**
	73.5 - 76.5	+454	+43	*

n: '76 = 82; '85 = 12; '90 = 3; '95 = 23

†at mid-point of length range



Historical vs 1995 Hg

Yr	Length Range	Difference† ng/g	Difference† %	Sig.
77	44.7 - 50.2	-29	-18	ns
	50.2 - 52.2	-48	-28	
	52.2 - 56.1	-64	-36	*
	56.1 - 83.8	-176	-80	**
82	42.9 - 57.3	+23	+10	ns
	57.3 - 67.8	-21	-7	ns

n: '77 = 22; '82 = 6; '95 = 15
†at mid-point of length range

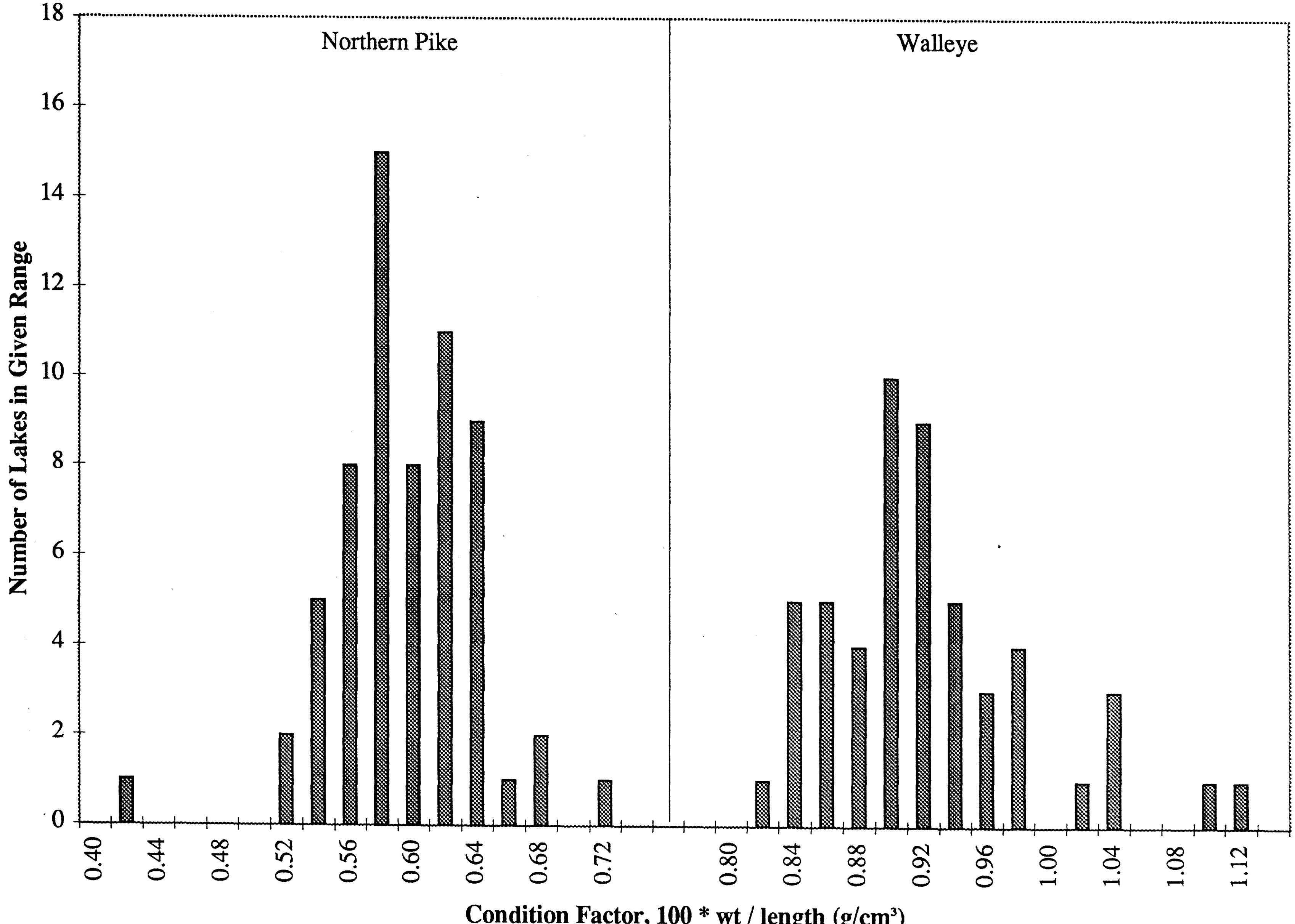


Figure 2.4. Histograms of average condition factors for northern pike and walleye for each study lake ('95 & '96 data).

Appendix

Appendix 1. Precipitation Database. Example page.

Appendix 2. Fish Bench-Mark Database. Example page.

Appendix 1. Precipitation Database. Example page.

Bethel	Hg Collection Year	day	tday	Seas.†	Hg Mod	Hg Conc (ppt)	Hg ‡‡ Mass (ng)	Net Volume (L)	Depth ‡‡ (cm)	Comments	Depth w/ Hg (cm)	Hg Depos (µg/m2)	Cum. Depos.	pres/diw	overflow & blank correctedY Hg depos	cum depos	cum dpth	conc.	Estimated†† Vol (L)	(Vm-Ve) /1.414	(Vm+Ve) /1.414	OUTLIERS* high	low1	low2	Deposition (ug/m2) depth based	bottle based	Depth w/o Hg	Ovflw‡ Problems	Grand depos	Grnd Depos Sum	Grnd Depth Sum	raw bottle results deposition	depth	blank corr conc	mass
1/9/90	90	9	9	W						P				12,40											0.000										
1/16/90	90	16	16	W						P				12,40											0.000										
1/23/90	90	23	23	W					0.076	P			0.0	12,40		0.0	0.0		0.076								0.076		0.01	0	0.1				
1/30/90	90	30	30	W					0.127	P			0.0	12,40		0.0	0.0		0.127								0.127		0.01	0	0.2				
2/6/90	90	37	37	W					0.305	P			0.0	12,40		0.0	0.0		0.305								0.305		0.03	0	0.5				
2/13/90	90	44	44	W			1.7	-0.004	0.000	T	0.000	0.000	0.0	12,40	0.00	0.0	0.0		0.000	-0.003	-0.003				0.000	0.000			0.00	0	0.5				0.8
2/20/90	90	51	51	W		6.8	4.4	0.648	0.508	T	0.508	0.027	0.0	12,40	0.03	0.0	0.5	5.4	0.508	0.099	0.817				0.027	0.035			0.03	0	1.0			5.4	3.5
2/27/90	90	58	58	W		10.5	9.7	0.926	0.635	T	0.635	0.061	0.1	12,40	0.06	0.1	1.1	9.5	0.635	0.206	1.104				0.061	0.088			0.06	0	1.7			9.5	8.8
3/6/90	90	65	65	W		653.7	1.8	0.003	0.000	T	0.000	0.000	0.1	12,40	0.00	0.1	1.1		0.000	0.002	0.002				0.000	0.009			0.00	0	1.7			332.3	0.9
3/13/90	90	72	72	W		9.2	18.9	2.048	6.121	T,OT	6.121	0.536	0.6	12,40	0.46	0.5	7.3	7.5	6.121	-2.880	5.776		1		0.536	0.180		2	0.46	1	7.8			8.8	18
3/20/90	90	79	79			6.8	13.9	2.048	1.803	T	1.803	0.115	0.7	12,40	0.11	0.7	9.1	6.0	3.624	-1.114	4.011				0.115	0.066		2	0.11	1	9.6			6.4	13
3/27/90	90	86	86				2.4	-0.010	0.000	T	0.000	0.000	0.7	12,40	0.00	0.7	9.1		0.000	-0.007	-0.007				0.000	0.000			0.00	1	9.6				1.5
4/3/90	90	93	93			7.7	10.9	1.418	0.838	T	0.838	0.059	0.8	12,40	0.06	0.7	9.9	7.1	1.684	-0.188	2.194				0.059	0.050			0.06	1	10.4			7.1	10
4/10/90	90	100	100			41.0	6.9	0.167	0.127	T	0.127	0.030	0.8	12,40	0.03	0.7	10.0	23.8	0.255	-0.062	0.299				0.045	0.030			0.03	1	10.5			35.6	6
4/17/90	90	107	107			19.0	10.9	0.576	0.381	T	0.381	0.066	0.9	12,40	0.07	0.8	10.4	17.4	0.766	-0.134	0.949				0.066	0.050			0.07	1	10.9			17.4	10
4/24/90	90	114	114			17.0	86.5	5.098	1.651	T	1.651	0.278	1.2	12,40	0.25	1.1	12.1	15.1	3.319	1.258	5.951	1			0.278	0.432			0.25	1	12.6			16.8	85.6
5/2/90	90	122	122			24.2	146.6	6.058	3.683	T,-1	3.683	0.886	2.1	12,40	0.76	1.8	15.7	20.7	7.403	-0.951	9.518				0.886	0.735			0.76	2	16.3			24.1	145.7
5/8/90	90	128	128			54.2	16.7	0.308	0.254	T	0.254	0.130	2.2	12,40	0.13	2.0	16.0	51.3	0.511	-0.143	0.579				0.130	0.080			0.13	2	16.5			51.3	15.8
5/15/90	90	135	135	S		12.3	60.6	4.912	2.794	T	2.794	0.339	2.5	12,40	0.31	2.3	18.8	10.9	5.616	-0.498	7.444				0.339	0.298			0.31	2	19.3			12.1	59.7
5/22/90	90	142	142	S		5.5	48.0	8.673	4.547	T	4.547	0.245	2.8	12,40	0.19	2.5	23.3	4.2	9.139	-0.330	12.595				0.245	0.235			0.19	3	23.9			5.4	47.1
5/29/90	90	149	149	S		17.4	52.5	3.019	1.854	T	1.854	0.317	3.1	12,40	0.31	2.8	25.2	16.5	3.727	-0.500	4.770				0.317	0.257			0.31	3	25.7			17.1	51.6
6/5/90	90	156	156	S		20.9	171.7	8.204	9.195	T,OB	9.195	1.912	5.0	12,40	0.84	3.6	34.4	9.1	18.482	-7.267	18.870		1		1.912	0.851		8	0.84	4	34.9			20.8	170.8
6/12/90	90	163	163	S		8.3	32.9	3.961	2.921	T	2.921	0.236	5.2	12,40	0.22	3.8	37.3	7.5	5.871	-1.351	6.952				0.236	0.160			0.22	4	37.8			8.1	32
6/19/90	90	170	170	S		5.4	47.2	8.697	7.569	T,OB	7.569	0.401	5.6	12,40	0.22	4.0	44.9	2.9	15.214	-4.608	16.908		1		0.401	0.231		8	0.22	4	45.4			5.3	46.3
6/26/90	90	177	177	S		12.3	13.2	1.078	0.635	T	0.635	0.073	5.7	12,40	0.07	4.1	45.5	11.5	1.276	-0.140	1.665				0.073	0.061			0.07	4	46.0			11.5	12.3
7/3/90	90	184	184	S		21.9	81.3	3.714	2.083	T	2.083	0.451	6.2	12,40	0.42	4.5	47.6	20.4	4.187	-0.334	5.587				0.451	0.401			0.42	5	48.1			21.7	80.4
7/10/90	90	191	191	S		15.7	54.6	3.474	1.905	T	1.905	0.294	6.5	12,40	0.28	4.8	49.5	14.7	3.829	-0.251	5.164				0.294	0.268			0.28	5	50.0			15.4	53.7
7/17/90	90	198	198	S		15.5	86.3	5.551	2.667	T	2.667	0.409	6.9	12,40	0.36	5.2	52.2	13.5	5.361	0.135	7.716				0.409	0.426			0.36	5	52.7			15.3	85.4
7/24/90	90	205	205	S		15.1	13.8	0.915	0.381	T	0.381	0.054	6.9	12,40	0.05	5.2	52.6	14.1	0.766	0.105	1.189				0.054	0.064			0.05	5	53.1			14.1	12.9
7/31/90	90	212	212	S		7.5	65.4	8.671	7.874	T,OB	7.874	0.582	7.5	12,40	0.31	5.5	60.4	3.9	15.827	-5.060	17.322		1		0.582	0.322		8	0.31	6	60.9			7.4	64.5
8/7/90	90	219	219	S		25.1	102.3	4.073	1.763	VG,T	1.763	0.439	7.9	12,40	0.41	5.9	62.2	23.1	3.544	0.374	5.386				0.439	0.505			0.41	6	62.7			24.9	101.4
8/14/90	90	226	226	S		24.4	7.5	0.308	0.300	VG,T	0.300	0.064	8.0	12,40	0.06	6.0	62.5	21.5	0.603	-0.209	0.644				0.064	0.033			0.06	6	63.0			21.5	6.6
8/21/90	90	233	233	S		8.5	154.7	18.149	8.677	VG,T	8.677	0.733	8.7	12,40	0.33	6.3	71.2	3.8	17.441	0.501	25.166				0.733	0.767			0.33	6	71.7			8.5	153.8
8/28/90	90	240	240	S		23.1	186.4	8.054	5.334	T	5.334	1.226	10.0	12,40	0.97	7.3	76.5	18.3	10.721	-1.886	13.276		1		1.226	0.925			0.97	7	77.0			23.0	185.5
9/4/90	90	247	247	S		19.8	46.0	2.318	0.991	T	0.991	0.192	10.2	12,40	0.19	7.5	77.5	19.2	1.992	0.231	3.048				0.192	0.225			0.19	8	78.0			19.4	45.1
9/11/90	90	254	254	S		19.0	36.8	1.937	1.016	T	1.016	0.188	10.3	12,40	0.19	7.7	78.5	18.5	2.042	-0.074	2.814				0.188	0.179			0.19	8	79.0			18.5	35.9
9/18/90	90	261	261	S		46.5	91.1	1.959	0.940	T	0.940	0.433	10.8	12,40	0.43	8.1	79.4	46.0	1.889	0.049	2.721				0.433	0.450			0.43	8	80.0			46.0	90.2
9/25/90	90	268	268	S		8.6	26.5	3.068	1.651	T	1.651	0.137	10.9	12,40	0.13	8.3	81.1	8.0	3.319	-0.177	4.516				0.137	0.128			0.13	8	81.6			8.3	25.6
10/2/90	90	275	275			55.2	17.5	0.318	0.178	T	0.178	0.093	11.0	12,40	0.09	8.4	81.3	52.4	0.358	-0.028	0.478				0.093	0.084			0.09	8	81.8			52.4	16.6
10/9/90	90	282	282		<	1.2	5.2	4.313	2.388	T	2.388	0.024	11.0	12,40	0.02	8.4	83.7	0.9	4.800	-0.344	6.444				0.024	0.022			0.02	8	84.2			1.0	4.3
10/16/90	90	289	289			15.1	16.8	1.118	0.635	T	0.635	0.091	11.1	12,40	0.09	8.5	84.3	14.3	1.276	-0.112	1.693				0.091	0.080			0.09	9	84.8			14.3	15.9
10/23/90	90	296	296			28.4	143.7	5.063	3.073	T	3.073	0.867	12.0	12,40	0.78	9.2	87.4	25.3	6.177	-0.788	7.948				0.867	0.720			0.78	9	87.9			28.2	142.8
10/30/90	90	303	303				3.8	-0.022	0.000	T	0.000	0.000	12.0	12,40	0.00	9.2	87.4		0.000	-0.016	-0.016				0.000	0.000			0.00	9	87.9				2.9
11/6/90	90	310	310		<	1.7	0.8	0.509	0.254	T	0.254	0.002	12.0	12,40	0.00	9.2	87.6	0.8	0.511	-0.001	0.721				0.002	0.000			0.00	9	88.1			0.8	0
11/13/90	90	317	317			58.7	9.2	0.156	0.279	T	0.279	0.042	12.0	12,40	0.04	9.3	87.9	15.0	0.561	-0.286	0.507				0.148	0.042			0.04	9	88.4			52.9	8.3
11/20/90	90	324	324				3.4	-0.022	0.102	T			12.0	12,40		9.3	87.9		0.205	-0.161	0.129			1		0.000	0.102		0.01	9	88.5				2.5
11/27/90	90	331	331			7.7	6.6	0.848	0.460	VG,T	0.460	0.031	12.1	12,40	0.03	9.3	88.4	6.6	0.925	-0.054	1.253				0.031	0.029			0.03	9	89.0			6.6	5.7
12/4/90	90	338	338	W	<	0.6	1.0	1.569	0.616	VG,T	0.616	0.005	12.1	12,40	0.00	9.3	89.0	0.8	0.616	0.674	1.545	1			0.005	0.001			0.00	9	89.6			0.8	0.1
12/11/90	90	345	345	W			1.4	-0.004	0.000	T	0.000	0.000	12.1	12,40	0.00	9.3	89.0		0.000	-0.003	-0.003				0.000	0.000			0.00	9	89.6				0.5
12/18/90	90	352	352	W	<	0.5	0.4	0.678	0.432	T	0.432	0.003	12.1	12,40	0.00	9.3	89.4	0.8	0.432	0.174	0.785				0.003	0.000			0.00	9	90.0			0.8	0
12/28/90	90	362	362	W		7.9	7.4	0.940	0.381	T,-3	0.381	0.026	12.1	12,40	0.03	9.3	89.8	6.9	0.381	0.395	0.934				0.026	0.065			0.03	9	90.4			6.9	6.5
12/31/90	90	365	365	W			2.7	-0.004	0.000	T	0.000	0.000	12.1	12,40	0.00	9.3	89.8		0.000	-0.003	-0.003				0.000	0.000			0.00	9	90.4				1.8
1/8/91	91	8	373	W			0.1	-0.002	0.000	T	0.000	0.000	12.1	12,40	0.00	9.3	89.8		0.000	-0.001	-0.001				0.000	0.000			0.00	9	90.4				0
1/15/91	91	15	380	W		11.2	7.7	0.688	0.635	T	0.635	0.063	12.2	12,40	0.06	9.4	90.4	9.9	0.635	0.037	0.936				0.063	0.068			0.06	9	91.0			9.9	6.8
1/22/91	91	22	387	W			1.5	-0.012	0.076	T			12.2	12,40		9.4	90.4		0.076	-0.062	0.045			1		0.000	0.076		0.01	9	91.1				0.6
1/29/91	91	29	394	W		9.0	4.4	0.488	0.229	T	0.229	0.016	12.2	12,40	0.02	9.4	90.7	7.2	0.229	0.183	0.507				0.016	0.035			0.02	9	91.3			7.2	3.5
2/5/91	91	36	401	W			1.2	-0.017	0.000	T	0.000	0.000	12.2	12,40	0.00	9.4	90.7		0.000	-0.012	-0.012				0.000	0.000			0.00	9	91.3				0.3
2/12/91	91	43	408	W			1.0	-0.026	0.000	T	0.000	0.000	12.2	12,40	0.00	9.4	90.7		0.000	-0.019	-0.019				0.000	0.000			0.00	9	91.3				0.1
2/19/91	91	50	415	W		3.5	4.4	1.237	0.889	OE,T	0.889	0.025	12.2	12,40	0.02	9.5	91.5	2.8	0.889	0.246	1.503				0.025	0.035			0.02	10	92.2			2.8	3.5
2/26/91	91	57	422	W		4.4	5.9	1.348	0.838	T	0.838	0.031	12.2	12,40	0.03	9.5	92.4	3.7	0.838	0.361	1.546				0.031	0.050			0.03	10	93.1			3.7	5
3/5/91	91	64	429	W		5.8	1.4	0.238	0.229	T	0.229	0.005	12.2	12,40	0.00	9.5	92.6	2.0	0.229	0.006	0.330				0.005	0.005			0.00	10	93.3			2.0	0.5
3/12/91	91	71	436	W		15.1	3.8	0.248	0.330	T	0.330	0.038	12.3	12,40	0.04	9.5	92.9	11.5	0.330	-0.058	0.409				0.038	0.029			0.04	10	93.6			11.5	2.9
3/19/91	91	78	443			24.0	1.9	0.078	0.127	T	0.127	0.005	12.3	12,40	0.01	9.5	93.1	4.0	0.255	-0.125	0.236				0.016	0.005			0.01	10	93.8			12.5	1

Appendix ... .sh Bench-Mark Database. Example page.

		digested	fish Hg	fish Hg	fish	fish					DNR													Hg @
		mass	conc	conc (ppb)	wt	len					determined age				logs			len						std
code	site	(mg)	(ppb)	corrected*	(g)	(cm)	id	sp	run	name	scale	scale dup	cleithra	best[a]	len	Hg		avg	SSX	slope	intcpt	syx	n	siz
F1381530961771P00	38153	232.3	507.1		1820	69.0	1	A1U	905	Adams	5	5		5	1.8	2.7		1.8	0.083	2.29	-1.5	0.078	11	315.5
F1381530961771P10	38153	256.4	202.2		861	52.6	2	A1U	905	Adams	3	3		3	1.7	2.3								
F1381530961771P20	38153	283.6	280.0		679	50.2	3	A1U	905	Adams	4	4		4	1.7	2.4								
F1381530961771P30	38153	242.3	355.8		1540	62.1	4	A1U	905	Adams	4	4		4	1.8	2.6								
F1381530961771P40	38153	276.6	498.1		2010	67.8	5	A1U	905	Adams	5	6		6	1.8	2.7								
F1381530961771P50	38153	273.8	248.1		488	43.7	16	A1U	905	Adams	2	2		2	1.6	2.4								
F1381530961771P60	38153	251.6	556.7		1805	66.5	6	A1U	906	Adams	5	6		6	1.8	2.7								
F1381530961771P70	38153	232.0	931.0		3570	84.8	12	A1U	906	Adams	7	7		7	1.9	3.0								
F1381530961771P80	38153	267.8	782.0		2820	80.5	13	A1U	906	Adams	6	7		7	1.9	2.9								
F1381530961771P90	38153	264.9	807.3		2885	80.0	18	A1U	906	Adams	7	7		7	1.9	2.9								
F1381530961771PA0	38153	262.7	342.7		1375	60.8	19	A1U	906	Adams	3	4		3	1.8	2.5								
F1381530961771P31	38153	268.4	332.1		1540	62.1	4	A1U	905	Adams	4	4		4	1.8	2.5								
F1381530961771P61	38153	233.7	538.5		1805	66.5	6	A1U	906	Adams	5	6		6	1.8	2.7								
F1381530961771P62	38153	240.6	516.8		1805	66.5	6	A1U	911	Adams	5	6		6	1.8	2.7								
F1381530961771P64	38153	258.2	597.2		1805	66.5	6	A1U	933	Adams	5	6		6	1.8	2.8								
F1381530961771P63	38153	305.2	519.8		1805	66.5	6	A1U	911	Adams	5	6		6	1.8	2.7								
F1166220961441P00	16622	246.7	175.0		1085	55.6	2	A1M	900	Alton	3			3	1.7	2.2		1.8	0.170	1.94	-1.1	0.151	10	201.3
F1166220961441P10	16622	235.0	114.1		850.0	49.5	5	A1F	900	Alton	2			2	1.7	2.1								
F1166220961441P20	16622	255.2	385.4		2620	71.5	6	A1M	900	Alton	5			5	1.9	2.6								
F1166220961441P30	16622	250.9	112.1		875.0	51.7	7	A1M	900	Alton	2			2	1.7	2.0								
F1166220961441P40	16622	234.2	230.5		1590	63.1	14	A1M	900	Alton	4			4	1.8	2.4								
F1166220961441P50	16622	244.5	488.6		2150	71.1	15	A1M	900	Alton	6			6	1.9	2.7								
F1166220961441P60	16622	229.5	490.2		3180	73.8	18	A1M	900	Alton	5			5	1.9	2.7								
F1166220961421P90	16622	241.3	81.6		108	27.0	1	AIU	939	Alton					1.4	1.9								
F1166220961441P70	16622	270.4	433.1		3950	78.8	23	A1M	900	Alton	6			6	1.9	2.6								
F1166220961441P80	16622	295.4	118.3		700.0	48.1	30	A1M	900	Alton	2			2	1.7	2.1								
F1698640951641B00	69864	221.3	205.4	181.0	430	42.5	89	A1F	872	Ash				2	1.6	2.3		1.7	0.043	1.31	0.15	0.138	10	266.0
F1698640951641B10	69864	228.6	172.8	152.2	420	40.8	90	A1M	872	Ash				2	1.6	2.2								
F1698640951641B20	69864	207.8	284.6	250.7	882	53.3	91	A1F	872	Ash				3	1.7	2.4								
F1698640951641B30	69864	242.9	202.1	178.1	1052	54.1	92	A1F	872	Ash				3	1.7	2.3								
F1698640951641B40	69864	204.9	389.1	342.8	1275	57.9	93	A1M	872	Ash				5	1.8	2.5								
F1698640951641B50	69864	242.0	360.4	317.5	2500	71.8	94	A1F	872	Ash				5	1.9	2.5								
F1698640951641B60	69864	237.5	249.4	219.7	568	47.0	104	A1M	872	Ash				3	1.7	2.3								
F1698640951641B70	69864	216.2	193.1	170.1	810	51.2	105	A1F	872	Ash				3	1.7	2.2								
F1698640951641B80	69864	225.0	482.6	425.2	992	52.2	106	A1M	872	Ash				3	1.7	2.6								
F1698640951641B90	69864	202.6	410.3	361.5	858	51.2	107	A1M	872	Ash				4	1.7	2.6								
F1698640951641B81	69864	230.3	497.7	438.5	992	52.2	106	A1M	872	Ash				3	1.7	2.6								
F1386910962391P00	38691	231.9	320.8		370.0	41.8	3	A1F	920	August	2			2	1.6	2.5		1.7	0.009	2.35	-1.4	0.146	6	533.8
F1386910962391P10	38691	289.8	192.9		370.0	40.6	6	A1F	920	August	2			2	1.6	2.3								
F1386910962391P20	38691	243.4	289.4		642.0	48.3	27	A1F	920	August	2			2	1.7	2.5								