ACRES CONSULTING SERVICES -
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CANADA CENTRE FOR INLAND WATERS
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ATMOSPHERIC LOADINGS OF THE UPPER GREAT LAKES

PHASE I

ABSTRACT

A review of emissions and atmospheric loadings in the Great Lakes Basin is given. A summary and critical discussion of regional models of atmospheric loading is included. Previous precipitation chemistry data are analyzed statistically to define relationships among variables.

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1 - INTRODUCTION

1 - INTRODUCTION

The Great Lakes Water Quality Agreement of April 15, 1972 between the United States and Canada reads on page 44 as follows:

"The Commission is requested to enquire into and to report to the two Governments upon the following questions:

(1) Are the waters of Lake Superior and Lake Huron being polluted on either side of the boundary to an extent (a) which is causing or likely to cause injury to health or property on the other side of the boundary; or (b) which is causing, or likely to cause, a degradation of existing levels of water quality in these two lakes or in downstream portions of the Great Lakes System?

(2) If the foregoing questions are answered in the affirmative, to what extent, by what causes, and in what localities is such pollution taking place?

(3) If the Commission should find that pollution of the character just referred to is taking place, what remedial measures would, in its judgment, be most practicable to restore and protect the quality of the waters, and what would be the probable cost?

(4) In the event that the Commission should find that little or no pollution of the character referred to is taking place at the present time, what preventive measures would, in its judgment, be most practicable to ensure that such pollution does not occur in the future and what would be the probable cost?"

It is recognized that determination of the ultimate fate of pollutants released artifically or naturally to the atmosphere is highly complex. This is especially true where many sources are grouped geographically and where the pollutants undergo chemical changes or interactions in the atmosphere. Nevertheless, precipitation chemistry studies in the Great Lakes region (McMaster University, and Canada Centre for Inland Waters (CCIW), and studies in continental United States (Lodge et al, Chemistry of United States Precipitation, National Centre for Atmospheric Research, Boulder, Colorado, August 1966, page 66, and Environment Science and Technology, 4, 1970, page 55) show that there is a marked definition of obvious sources and they show that the rate of loading from the atmosphere for the Upper Lakes

is probably the major contributor of metals and nutrients. Indeed, the concentration of $SO_4^=$ ion in rainfall, an approximately conservative substance, is twice the concentration of $SO_4^=$ in Lake Superior. Similarly, nutrients in precipitation exceed stream loadings by at least an order of magnitude (Sundridge conference notes of Kramer, Conroy and Shiomi, 1973). In the next few decades the water quality of the Upper Lakes may depend almost entirely on atmospheric loading. The large scale of the lakes and the long residence time (circa 100 years) so far has masked the effect of the pollution in water quality.

There is a variable amount of apparently mismatched data available for evaluation of loading on the Upper Great Lakes. In Ontario there are some 2 to 3 years of total fall data for the northern half of Lake Huron, and one season of ship data to correlate with the shore data. The stations of Lake Superior have been in operation onshore from about 1972 on and there appears to be a reasonable amount of ship data (60 stations) plus island analyses to verify and interconnect data. A preliminary survey of the United States literature suggests that there are numerous short-term programs that have not been connected. The most ambitious and long-range appears to be that in the Agriculture Department of Michigan State University, but only pH has been measured.

Two principal objectives are stated in the Terms of Reference for this project as follows:

(1) To evaluate the relationship between materials collected in shoreline and ship-based precipitation samplers so that the shoreline samples can be interpreted in terms of the lake surface loading;

(2) To develop a program whose goal is the determination of the sources or source regions of the materials contained in the precipitation over the Upper Great Lakes (Lakes Superior and Huron, and Georgian Bay) and to carry out such proposed program.

To meet these objectives the following items of work have been carried out or initiated in the Phase One of this ongoing project. The status of these items are reported in subsequent sections. Principal work tasks include:

(a) Collection of existing major source and area emissions data in and near the Upper Lakes (Superior, Huron, Georgian Bay) in Ontario and the Great Lakes States for computer storage and conversion of these to a standard 1973 base year.

(b) Collection of all available precipitation chemistry data in the Upper Lakes Basins for 1972 and 1973, including shipboard data for 1973, for computer storage.

(c) Collection of meteorological data on daily wind speeds and directions (surface for 1972 and 1973 and 850 mb for 1973), daily precipitation types and intensities and daily analysis of air mass type and synoptic weather conditions for 1972 and 1973, estimates of seasonal average mixing depths and Pasquill stability classifications by air mass for computer storage.

(d) Factor analyses of the 1972 and 1973 meteorological and chemistry data in computer storage to identify related and non-related variables.

(e) Review of existing mathematical models of regional air pollution transport, diffusion and deposition. Modification of the Slade model for the Washington-Boston region for use in Phase Two.

(f) Design of the Phase Two ongoing work program.

Arrangements for provision of a number of climatological and ongoing meteorological data sets were made with the Atmospheric Environment Service, Environment Canada, and the National Oceanographic and Atmospheric Authority, United States. Agencies supplying precipitation chemistry data include the Canada Centre for Inland Waters, the Atmospheric Environment Service, the Ontario Air Management Branch, the Michigan Department of Natural Resources, the United States Environmental Protection Agency, The Wisconsin Department of Natural Resources.

Agencies providing air emissions data include the Ontario Air Management Branch and The Federal Air Pollution Control Directorate in Canada, the appropriate State agencies in New York, Pennsylvania, Ohio, Michigan, Indiana, Illinois and Wisconsin and the Environmental Protection Agency in the United States. The co-operation of all of these agencies is gratefully acknowledged.

2 - PRECIPITATION CHEMISTRY AND CLIMATOLOGICAL DATA

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Purpose

(1) To obtain a data file for precipitation chemistry concentration and loading (mass/area/time) data for CCIW and McMaster monthly snow and rain collectors in the Upper Great Lakes.

(2) To obtain a daily weather file of weather stations and to develop a synoptic weather file.

Locations

The precipitation chemistry network data file (CAPØ) consists of 23 stations in the Lakes Huron and Superior network in the Province of Ontario. This number will increase with the addition of the Michigan network.

The climatological data file (MET) consists of 11 first order weather stations representative of potential source areas and of the receptor areas, in addition to a daily synoptic record.

Figure 1 is a sketch map of the precipitation chemistry/weather stations. Table 1 gives the name and location of the stations. For identification purposes McMaster stations fall between 1 and 100, CCIW stations between 101 and 200, and Michigan EPA stations fall between 201 and 300.

Data Files

The precipitation chemistry data files are structured on a chronological basis with sorting by increasing parameter code with each station record. The file allows data to be flagged and each station record to carry commentary. Various switches allow the deletion of flagged data, etc. A calculation switch allows loadings to be determined from

$$L = C\ V/(A\Delta t)$$

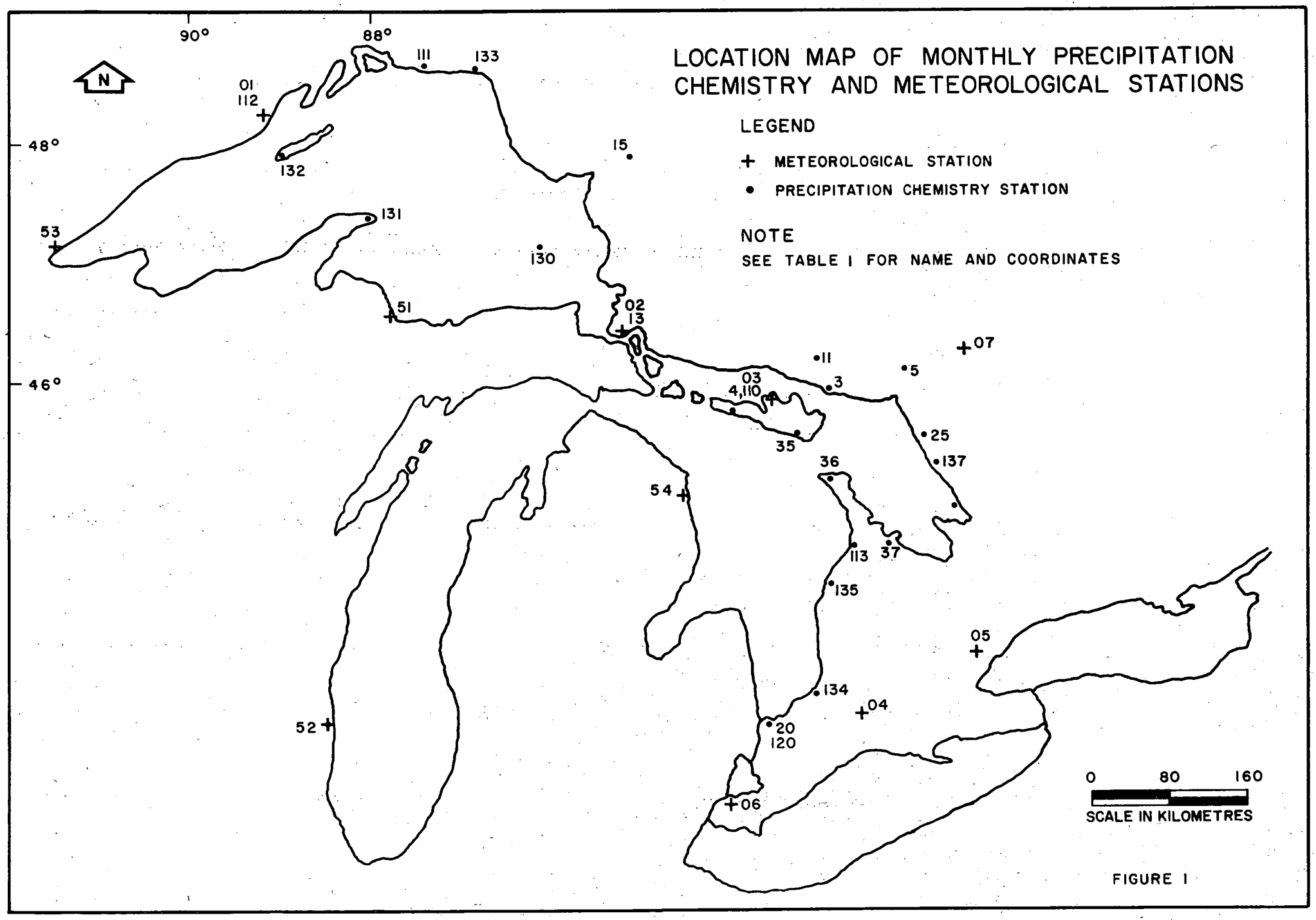

LOCATION MAP OF MONTHLY PRECIPITATION CHEMISTRY AND METEOROLOGICAL STATIONS
LEGEND
+ METEOROLOGICAL STATION
• PRECIPITATION CHEMISTRY STATION
NOTE
SEE TABLE I FOR NAME AND COORDINATES
N
90°
88°
48°
46°
01
112
132
53
131
130
51
02
13
15
111
133
11
3
5
07
03
4,110
35
36
25
137
54
113
37
135
05
134
04
20
120
52
06
0
80
160
SCALE IN KILOMETRES

FIGURE I

TABLE 1

LOCATION OF MONTHLY CLIMATOLOGICAL AND PRECIPITATION STATIONS

Number	Name	Longitude	Latitude
Climatological Stations			
01	Thunder Bay, Ontario (Airport)	89-19	48-21
02	Sault Ste. Marie, Ontario	84-20	46-31
03	Gore Bay, Ontario (Airport)	82-27	45-53
04	London, Ontario (Airport)	81-09	43-01
05	Toronto, Ontario (Airport International)	79-39	43-40
06	Windsor, Ontario (Airport)	83-09	43-02
07	North Bay, Ontario (Airport)	79-27	46-19
51	Marquette, Michigan	87-24	46-32
52	Milwaukee, Wisconsin	87-54	42-01
53	Duluth, Minnesota	92-06	46-48
54	Alpena, Michigan	83-26	45-05
Precipitation Stations			
3	Killarney, Ontario	81-28	45-59
4	Gore Bay, Ontario	82-27	45-53
5	Jamot (Alban), Ontario	80-32	46-06
11	Espanola, Ontario	81-45	46-15
13	Sault Ste. Marie, Ontario	84-20	46-31
15	Wawa, Ontario	84-32	48-03
20	Sarnia, Ontario (Airport)	82-17	42-59
25	Shawanaga, Ontario	80-15	45-31
35	South Baymouth, Ontario	82-01	45-35
36	Cypress Provincial Park, Ontario (Tobermory)	81-35	45-14
37	Owen Sound, Ontario	80-53	44-33
110	Gore Bay, Ontario (Airport)	82-27	45-53
111	Schreiber, Ontario	87-16	48-48
112	Thunder Bay, Ontario (Airport)	89-19	48-21
113	Wiarton, Ontario (Airport)	81-14	44-39
120	Sarnia, Ontario (Airport)	82-17	42-59

Table 1 (Cont'd)

Number	Name	Longitude	Latitude
130	Caribou Island, Ontario	85-50	47-22
131	Copper Harbor, Michigan	87-53	47-27
132	Isle Royale, Michigan (Washington Landing)	89-07	47-51
133	Ney Provincial Park, Ontario	86-34	48-45
134	Pinery Provincial Park, Ontario	81-48	43-14
135	Inverhuron Park, Ontario	81-34	44-18
137	Kilbear Provincial Park, Ontario	80-12	45-21

Where L = loading (mass/area/time)

C = concentration (mass/volume)

V = volume of sampler

A = cross-sectional area of the sampler, and

Δt = the time interval of sampling.

Each parameter has a code, a value, and a flag (blank is normal). Code 123, pH, is handled in a special way in that the H^+ concentrations (10^{-pH}) are carried through all calculations and then converted back to pH; and if a log transform switch is active, it is by-passed for pH.

The structure of the concentration and data files is:

(a) File title and annotations.

(b) Gross statistics (mean, maximum, minimum, standard deviation, sample size) for the entire file.

(c) Statistics for each station for entire data file.

(d) Period data: statistics for a period, and data by station.

A library of code names, acronym for each variable, unit of concentration, and significant figure is part of the CAPØ system.

The MET system is somewhat similar to the CAPØ structure. At present it is being used as a separate data file. The MET file is chronologically structured with a secondary sorting on station. For these purposes the synoptic data are given the station value 0 and form the first record in the daily record. Table 2 is a summary of the MET data file.

Neither the CCIW nor climatological data files have been verified for accuracy of data at present.

TABLE 2

INDEX TO METEOROLOGICAL DATA

Synoptic Data (2): One Daily Record for Region

Air Mass:
- MT - Maritime Tropical
- MP - Maritime Polar
- MA - Maritime Arctic
- CA - Continental Arctic

Synoptic:
- WF - Warm Front
- WS - Warm Sector
- CF - Cold Front
- LM - Moving Low
- LS - Stagnant Low
- HM - Moving High
- HS - Stagnant High

Synoptic Data are Listed as Station 00

Daily Weather: One Daily Average Record for 11 Stations (Table 1)

Station Name
Date
Precipitation
Duration (L,M,H)
Kind of Precipitation (R,S,H,D)
Wind Speed
Direction

3 - ANALYSIS OF DATA

3 - ANALYSIS OF DATA

Introduction

At present monthly data for 1972-1973 from 23 shore stations in Lakes Huron and Superior have been analyzed. In addition, there are 43 samples taken from ships (38 in Superior and 5 in Huron), representing about 29 meteorological events for analysis. The ship samples can be analyzed for concentration only.

Purpose

Analysis was carried out for the following purposes:

On Monthly Samples

(1) What is the nature of the distributions of commonly analyzed parameters?

(2) What groupings of parameters exist as determined by factor analysis? What is the significance of the groupings?

(3) What stations have similar loadings of multivariables as determined by discriminant function analysis?

(4) What is the between group variance of McMaster-CCIW analyses as determined for data at Gore Bay, Ontario?

(5) What is the loading distributions of commonly measured parameters?

(6) What is the present best estimate of yearly loadings on Lake Huron and Lake Superior?

(7) Do the data show a source trend when they are weighted by wind direction, distance to source, precipitation events and analyzed by least squares?

On Event Samples

(1) What is the nature of distributions for commonly analyzed parameters?

(2) What is the coefficient of washout for various parameters during a precipitation event?

(3) Is there a grouping of event analyses by location?

TABLE 3

MOMENT ANALYSIS OF MONTHLY CONCENTRATION AND LOADING DATA - DATA LESS THAN OR EQUAL TO 0 ARE EXCLUDED

Concentration: McMaster Data

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
Cd F	89	2.7	2.0	19.5	1.7
log(10)	89	.23	-.08	.19	.48
Cd T	93	10.4	2.6	33.6	3.2
log(10)	93	.27	-.34	3.4	.52
Cu F	99	47.6	.66	1.4	6.9
log(10)	99	.24	-.48	1.4	.49
Cu T	109	357	1.05	4.4	19
log(10)	109	.25	-.15	-.07	.5
Fe F	92	12000	3	44	108
log(10)	92	.25	.07	.83	.5
Fe T	115	867000	1.7	11.8	931
log(10)	115	.24	.25	1.4	.49
Pb F	112	180	.29	-.17	13.4
log(10)	112	.16	-.88	5.3	.4
Pb T	118	1200	2.1	26	34.7
log(10)	118	.13	-.05	.48	.36
Ni F	93	25.2	1.5	11	5
log(10)	93	.15	.06	-.01	.39
Ni T	91	6500	4.5	83	81
log(10)	91	.28	.26	2	.53
Zn F	114	307000	3.8	63	554
log(10)	114	.16	.46	2.4	.4
Zn T	119	304000	3.4	55	552
log(10)	119	.19	.31	1.5	.43
SP CON	131	633	.82	3.1	25
log(10)	131	.05	.06	.41	.22
pH	135	.70	-.61	.44	.84
F	30	4200	.59	.76	65
log(10)	30	.33	-.25	-.6	.57
Cl	77	877000	.91	4	937
log(10)	77	.27	-.23	.07	.52
Br	85	302	.68	2.5	17.4
log(10)	85	.17	-.43	.71	.41
SO4	113	25.6	.93	3.5	5.1
log(10)	113	.13	-.5	3.9	.36
T PART	119	.00	2.4	30	.04
log(10)	119	.23	.06	.82	.48

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
K F	97	.11	1.4	9.8	.33
log(10)	97	.15	.12	.72	.38
MgF	27	.15	.98	3.5	.39
log(10)	27	.27	-.07	-.02	.52
Ca F	101	1.3	1.3	9	1.1
log(10)	101	.15	.07	.33	.39
ALK F	55	18.4	.8	4.6	4.3
log(10)	55	.08	-.29	.5	.28
T PO4 F	107	4100	2	18	64
log(10)	107	.16	.33	1.2	.4
T PO4	89	10000	.88	2.9	101
log(10)	89	.12	.13	-.71	.35
concentrations CCIW data Upper Lakes Stations					
Cd T	49	1.2	1.0	4.4	1.1
log(10)	49	.05	.59	.26	.22
Cu T	153	63.4	3.9	77.2	8.0
log(10)	153	.13	.30	.78	.36
Fe T	153	768	2.5	34.1	27.7
log(10)	153	.28	-.01	-.43	.53
Pb T	150	156	1.9	20.9	12.5
log(10)	150	.21	.07	-.56	.46
Ni T	118	14.1	3.1	50.7	3.8
log(10)	118	.09	.44	1.1	.31
Zn T	155	3094	1.1	5.4	55.6
log(10)	155	.16	-.03	-.18	.39
SP CON	170	1399	2.0	22.0	37.4
log(10)	170	.07	.37	.92	.27
pH	151	1.4	.42	1.0	1.2
SO4	167	3627042	1.0	4.6	1904
log(10)	167	.21	-.11	-.40	.46
Cl	158	12.9	1.0	5.7	3.6
log(10)	158	.06	-.09	1.2	.25
Na T	163	1.7	1.4	10.1	1.3
log(10)	163	.32	-.34	.37	.56
K T	165	14.4	6.2	157	3.8
log(10)	165	.21	.54	3.6	.46
Mg T	147	.19	1.4	9.5	.44
log(10)	147	.12	.09	-.39	.35
Ca T	156	7.5	1.4	10.0	2.7
log(10)	156	.18	-.16	.50	.42
ALK F	103	60.0	1.1	6.1	7.7
log(10)	103	.27	-.12	-.56	.52
Si O2	158	7.7	1.7	20.1	2.8
log(10)	158	.50	-.23	-.50	.70

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
TPO4	167	716025	3.1	43.0	846
log(10)	167	.32	.62	1.6	.56
PO4 R	175	318288	2.7	32.3	564
log(10)	175	.57	.60	.95	.76
N T	86	1.8	1.2	8.1	1.4
log(10)	86	.10	-.04	.51	.31
NO3 R	175	.96	1.8	15.3	.98
log(10)	175	.14	-.15	2.2	.38
NH3 R	174	1.2	2.3	24.9	1.1
log(10)	174	.15	-.10	5.2	.39
Loading: McMaster					
Cd F	89	.27	2.7	36.4	.52
log(10)	89	.33	.09	-.35	.58
Cd T	93	.85	3.1	44.7	.92
log(10)	93	.34	-.23	2.9	.59
Cu F	99	3.3	1.9	18.6	1.8
log(10)	99	.28	-.64	3.7	.53
Cu T	109	11.5	1.7	16.2	3.4
log(10)	109	.23	-.13	.42	.48
Fe F	92	1301	4.3	76.9	36.1
log(10)	92	.29	.07	1.1	.54
Fe T	115	45041	2.7	33.8	212
log(10)	115	.25	.27	1.1	.50
Pb F	112	19.3	1.0	5.1	4.4
log(10)	112	.26	-.62	2.6	.51
Pb T	118	31.9	1.5	12.9	5.6
log(10)	118	.15	-.21	.30	.39
Ni F	93	1.2	2.2	25.9	1.1
log(10)	93	.16	.07	.46	.40
Ni T	91	41.9	3.6	56.6	6.5
log(10)	91	.24	.26	1.2	.49
Zn F	114	2674	3.1	50.2	51.7
log(10)	114	.14	.24	1.1	.37
Zn T	119	2884	2.7	38.2	53.7
log(10)	119	.15	.09	1.2	.39
SP CON	131	45.6	1.2	9.0	6.7
log(10)	131	.11	-.31	1.5	.34
pH	135	1.0	-.61	.82	1.0
F	30	367	1.4	7.1	19.1
log(10)	30	.47	-.12	-.10	.69
Cl	77	23565	.81	2.5	154
log(10)	77	.32	-.44	1.3	.57

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
Br	85	18.3	.88	4.1	4.3
log(10)	85	.25	-.40	.50	.50
SO4	113	1.4	1.1	5.4	1.2
log(10)	113	.18	-.41	2.2	.43
T PART	119	0	1.4	9.8	.005
log(10)	119	.20	-.07	.08	.45
Cu T	12	.04	.78	2.1	.21
log(10)	12	.26	-.13	.71	.51
Zn FA	13	1182	1.5	9.1	34.4
log(10)	13	.14	.45	2.5	.38
Na F	92	.19	2.3	26.2	.43
log(10)	92	.40	.27	.51	.63
K F	97	.004	1.3	7.4	.06
log(10)	97	.19	-.13	.57	.44
Mg F	27	0	1.2	6.2	.06
log(10)	27	.22	-.01	.26	.47
Ca F	101	.04	1.3	8.2	.21
log(10)	101	.18	-.22	1.8	.42
ALK F	55	2.1	1.5	12.4	1.5
log(10)	55	.13	-.12	.71	.36
TPO4 F	107	202	1.6	11.4	14.2
log(10)	107	.25	.14	-.03	.50
Si O2	11	0	1.1	5.4	.05
log(10)	11	.21	.06	.20	.46
NO3 F	11	0	-.07	-.55	.04
log(10)	11	.08	-.60	1.7	.27
TPO4	89	781	1.0	4.1	27.9
log(10)	89	.18	.15	-.59	.42
CCIW Loading					
Cd T	49	.26	1.4	10.2	.51
log(10)	49	.15	.16	-.63	.38
Cu T	153	3.2	2.1	21.8	1.8
log(10)	153	.19	.13	-.07	.43
Fe T	153	65.1	2.3	29.7	8.1
log(10)	153	.34	.02	-.32	.58
Pb T	150	12.4	1.5	11.4	3.5
log(10)	150	.27	.06	-.58	.52
Ni T	118	3.1	4.2	78.2	1.8
log(10)	118	.14	.33	1.7	.38
Zn T	155	351	1.4	8.3	18.7
log(10)	155	.22	-.07	.21	.47

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
SP CON	170	44.9	1.3	8.8	6.7
log(10)	170	.10	-.60	6.9	.32
pH	151	1.7	.48	2.4	1.3
SO4	167	174425	1.2	7.2	418
log(10)	167	.21	-.15	-.11	.46
Cl	158	1.1	2.4	37.8	1.1
log(10)	158	.08	-.21	2.1	.29
Na T	163	.07	1.1	5.6	.26
log(10)	163	.34	-.49	.78	.58
K T	165	.19	5.6	134	.43
log(10)	165	.23	.37	2.0	.47
Mg T	147	.01	1.9	19.9	.11
log(10)	147	.14	-.07	.38	.37
Ca T	156	.39	1.6	13.6	.62
log(10)	156	.20	-.30	.90	.44
ALK F	103	2.6	1.2	6.9	1.6
log(10)	103	.22	-.07	-.42	.47
Si O2	158	.47	1.7	17.5	.69
log(10)	158	.62	-.41	.89	.79
TPO4	167	63172	3.3	52.2	251
log(10)	167	.35	.65	1.9	.60
PO4 R	175	27709	2.9	38.7	166
log(10)	175	.66	.52	.99	.82
N T	86	.14	1.4	10.3	.37
log(10)	86	.21	-.65	3.9	.45
NO3 R	175	.06	2.1	22.9	.24
log(10)	175	.23	-.70	5.3	.48
NH3 R	174	.11	2.4	26.5	.33
log(10)	174	.25	-.38	4.4	.50

Concentration Event Data
CCIW Data

* No variable size on printout

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
P T	*	1069.9	1.2	6.9	32.7
log(10)		.18	-.50	2.2	.42
N T		1689455	1.4	10.7	1300
log(10)		.05	.06	.55	.23
ALK		2007194	.30	.13	1417
log(10)		.18	-.57	1.3	.42
P R		8769	2.7	30.5	93.6
log(10)		.37	.10	-.15	.61
NO3		91114	.92	3.6	302
log(10)		.11	-.05	-.25	.33
NH3		52350100	3.1	38.1	7235
log(10)		.23	.93	5.8	.48
Cl		6982605	1.5	10.8	2642
log(10)		.15	.27	.24	.39
Si O2		6314	1.4	9.3	79.5
log(10)		.13	.13	.64	.36

(4) Is there a grouping of event analyses by wind direction?

(5) What is the between group variance for monthly shore data compared with shipboard event data?

3.1 - Monthly Data, Moment Analysis and Distributions

Data for CCIW and McMaster were analyzed for Second, Third and Fourth Moments about the mean for commonly measured parameters, and plots on cumulative probability paper were carried out for log(10) transforms of concentration and loading data to ascertain whether the data approximated a lognormal distribution. Table 3 is a summary of the moment analysis for log transform and for data with no transgenerations. The moments are Gaussian statistics and are defined by:

$$\text{Mean } X_n = \sum_i (x_i - \bar{x})^n$$

$$\text{Second Moment (variance) } m_2 = X_2/(n-1)$$

$$\text{Skewness } m_3 = X_3/(2(n-2)(s^3))$$

$$\text{Kurtosis } m_4 = X_4/((n-4)(s^4))-3$$

$$\text{Standard deviation } s = m_2^{\frac{1}{2}}$$

where x_i is a data point for the mean $\bar{x}$ of n samples, m_2, m_3, and m_4 are moments, and s is the standard deviation, m_3 and m_4 give zero values for a standard normal distribution.

Figures 2(a) to 2(r) are cumulative curve plots for all concentration and loading data for all parameters that are commonly analyzed. It is quite apparent that the distributions are lognormal, with little deviation. This conclusion is also apparent by noting that m_3 and m_4 in Table 3 are very nearly zero -- pH is perhaps an exception to this conclusion.

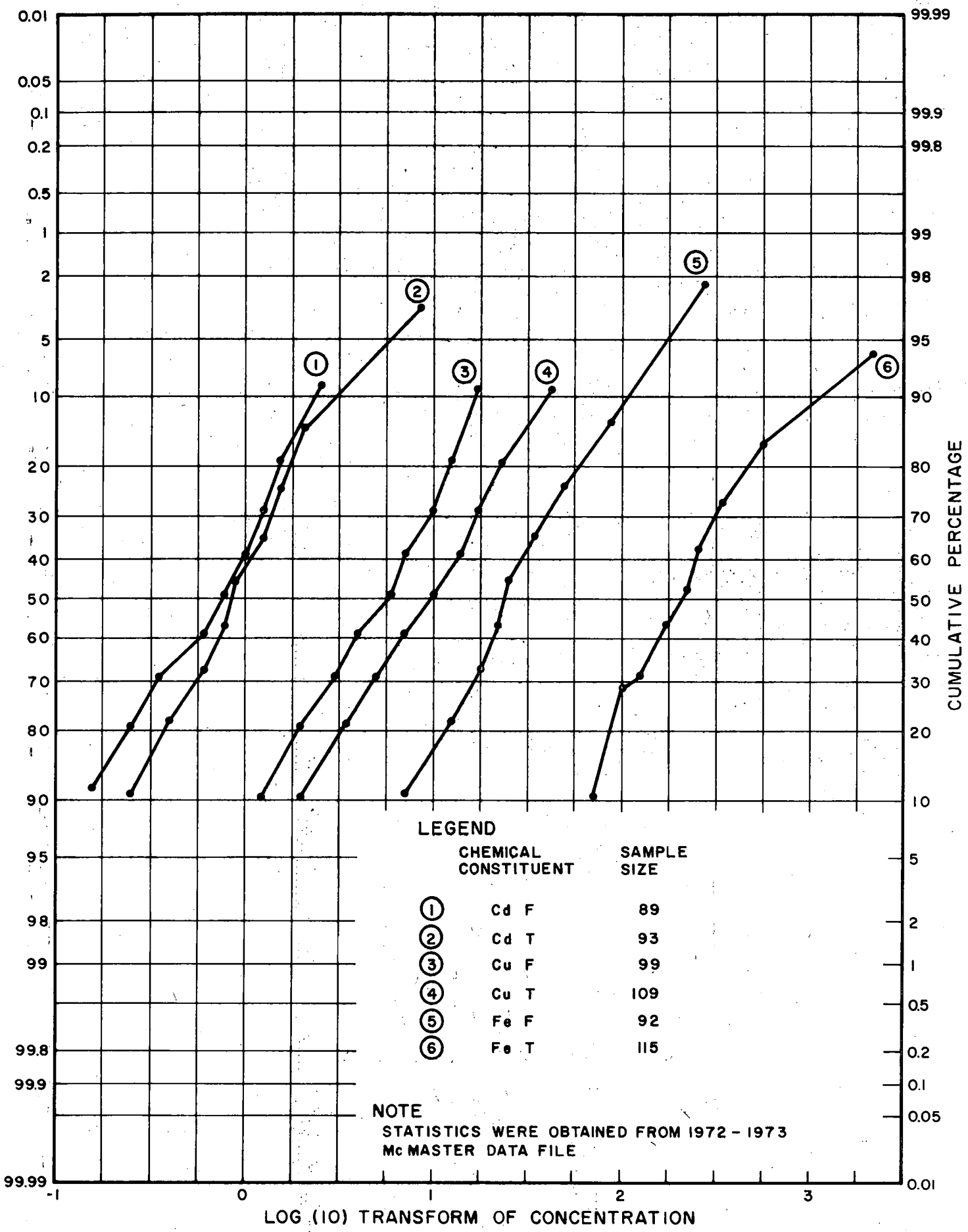


FIGURE 2 (a)

UPPER LAKES - CONCENTRATIONS

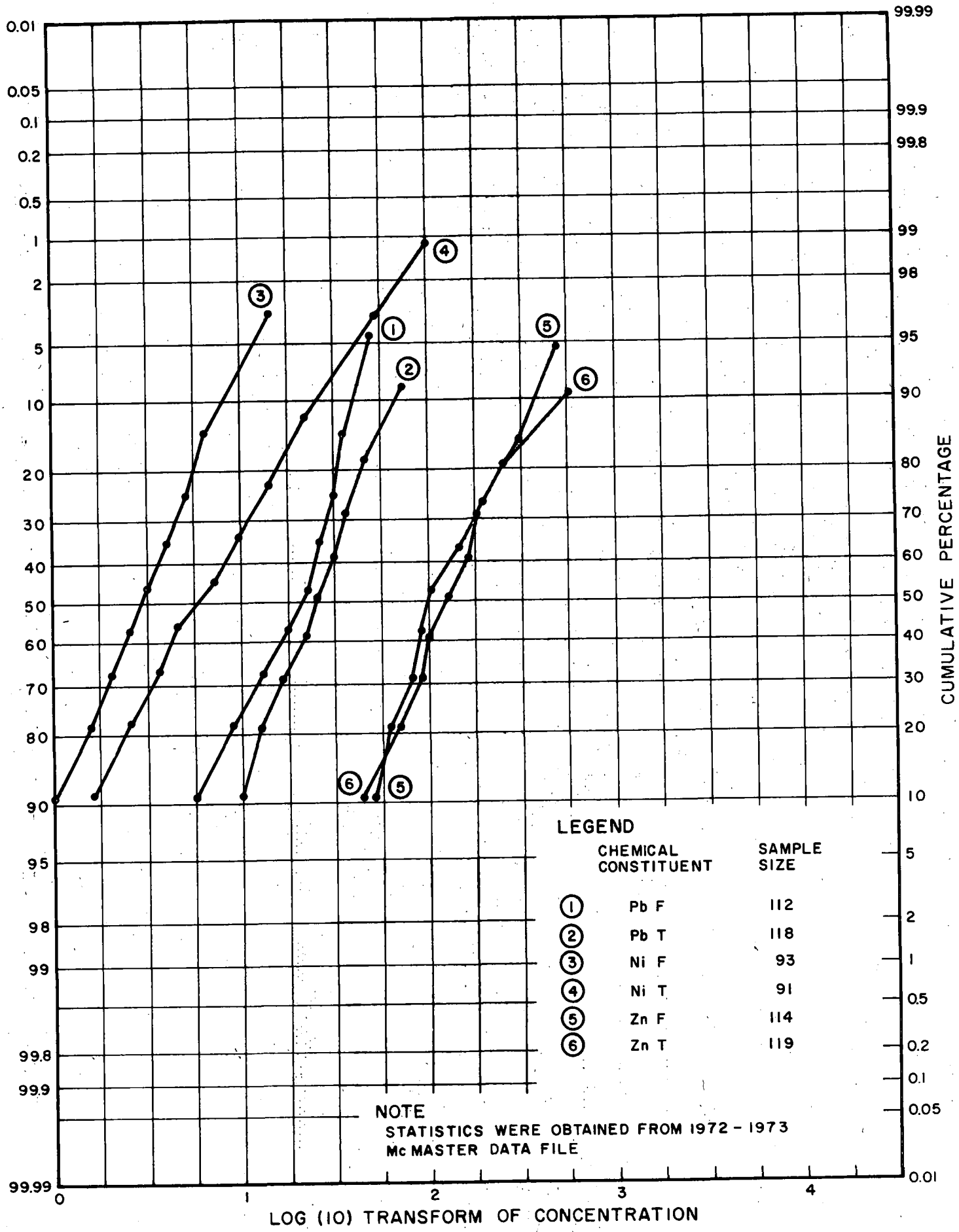


FIGURE 2 (b)

UPPER LAKES - CONCENTRATIONS

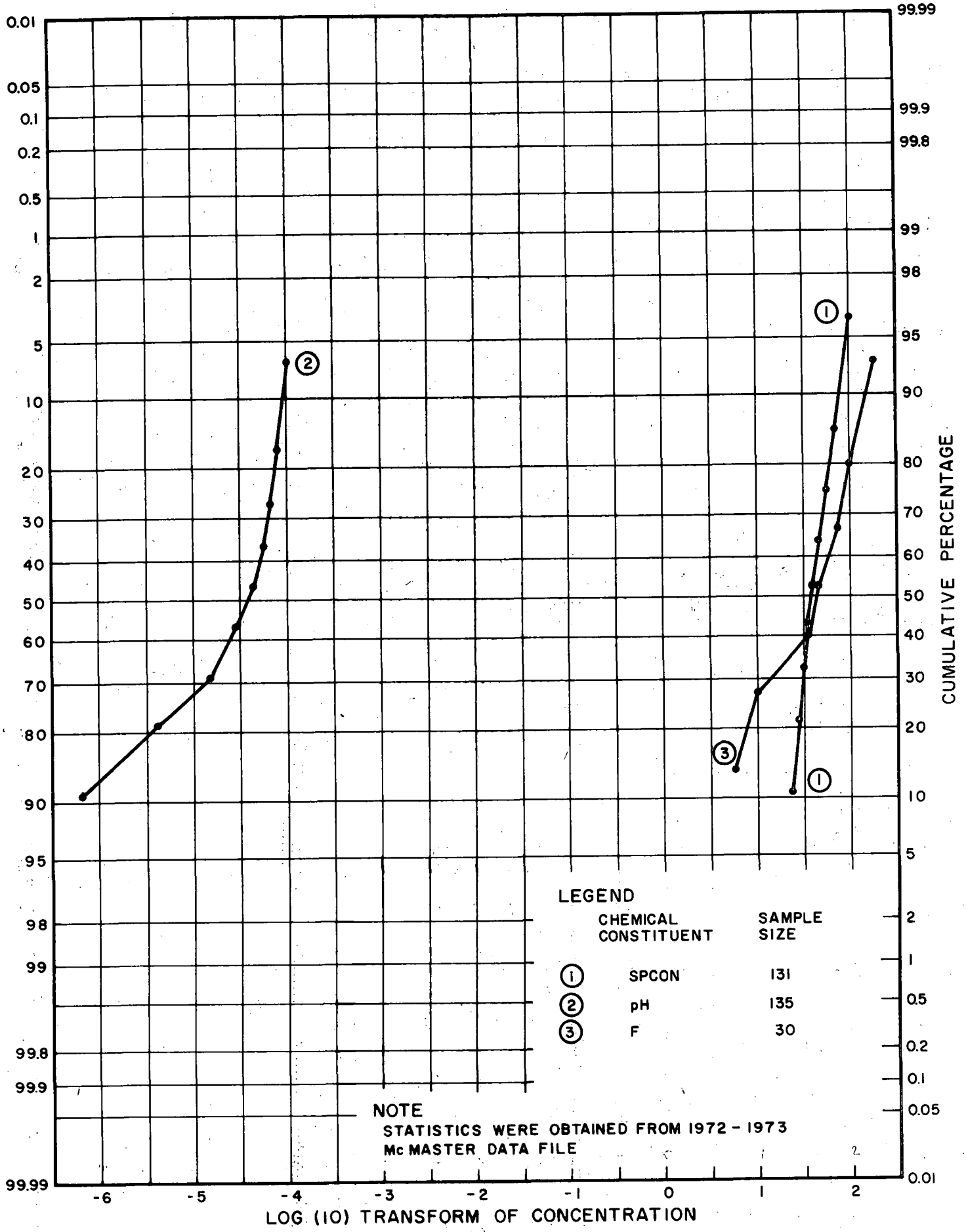


FIGURE 2 (c)

UPPER LAKES - CONCENTRATIONS

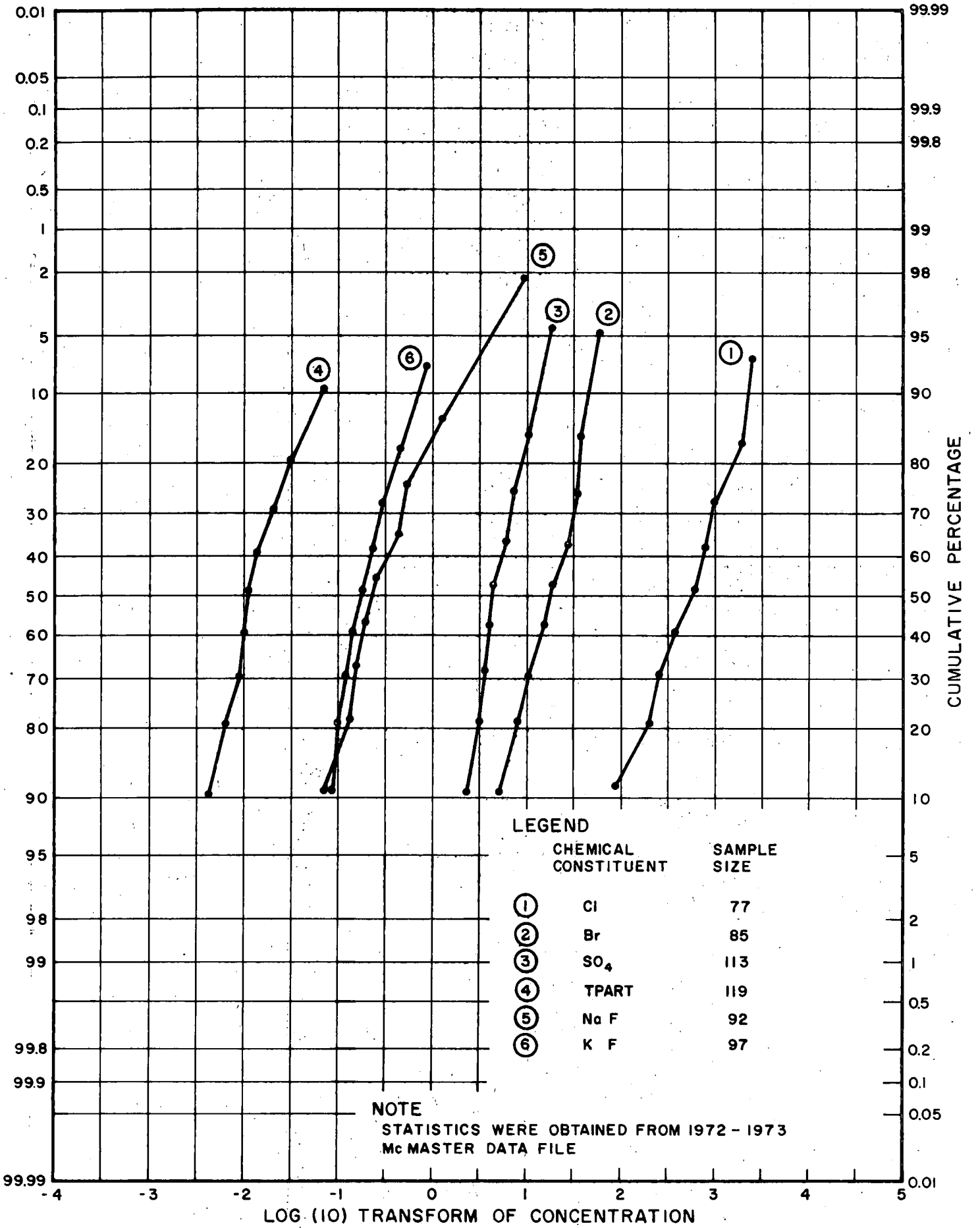


FIGURE 2 (d)

UPPER LAKES - CONCENTRATIONS

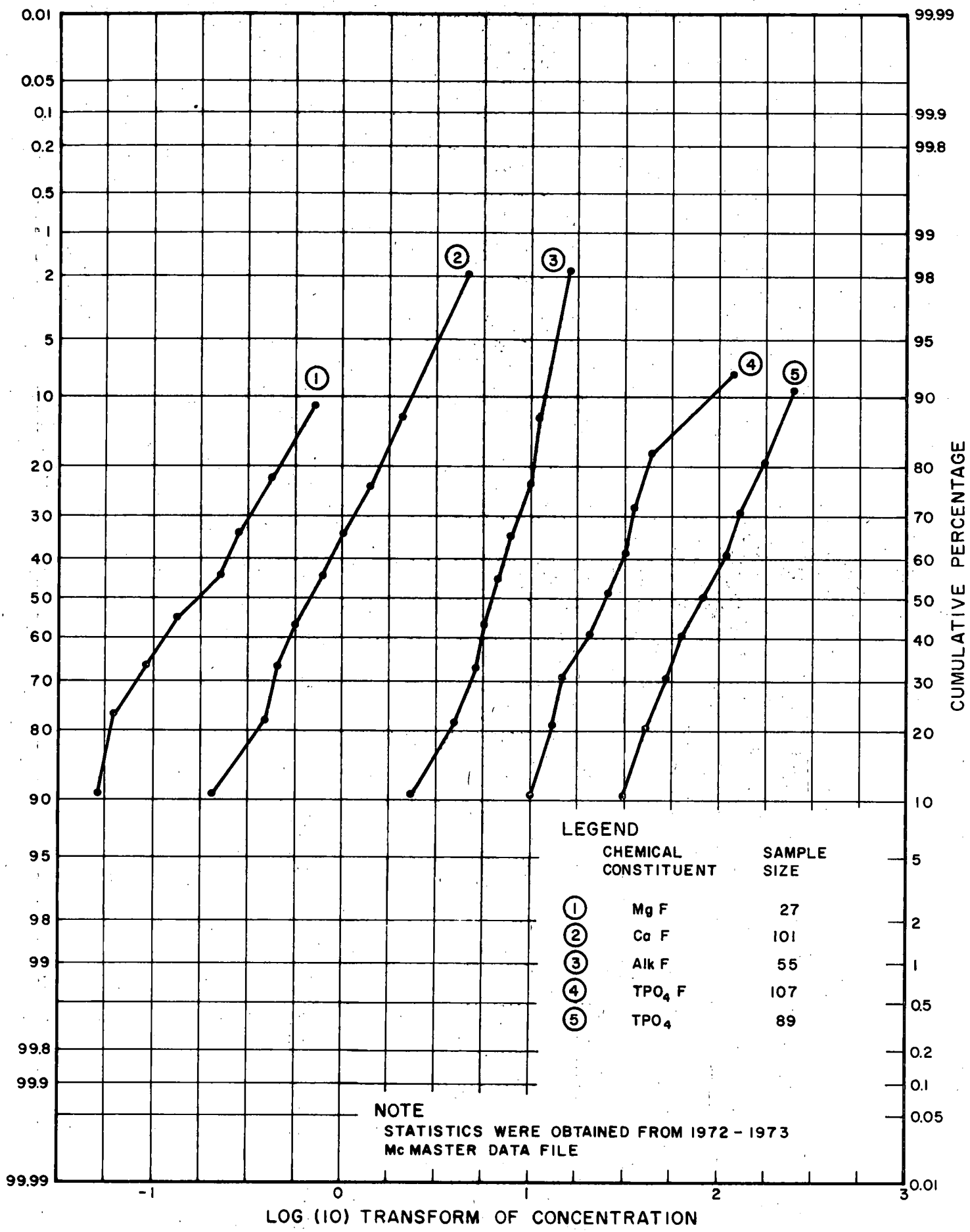


FIGURE 2 (e)

UPPER LAKES - CONCENTRATIONS

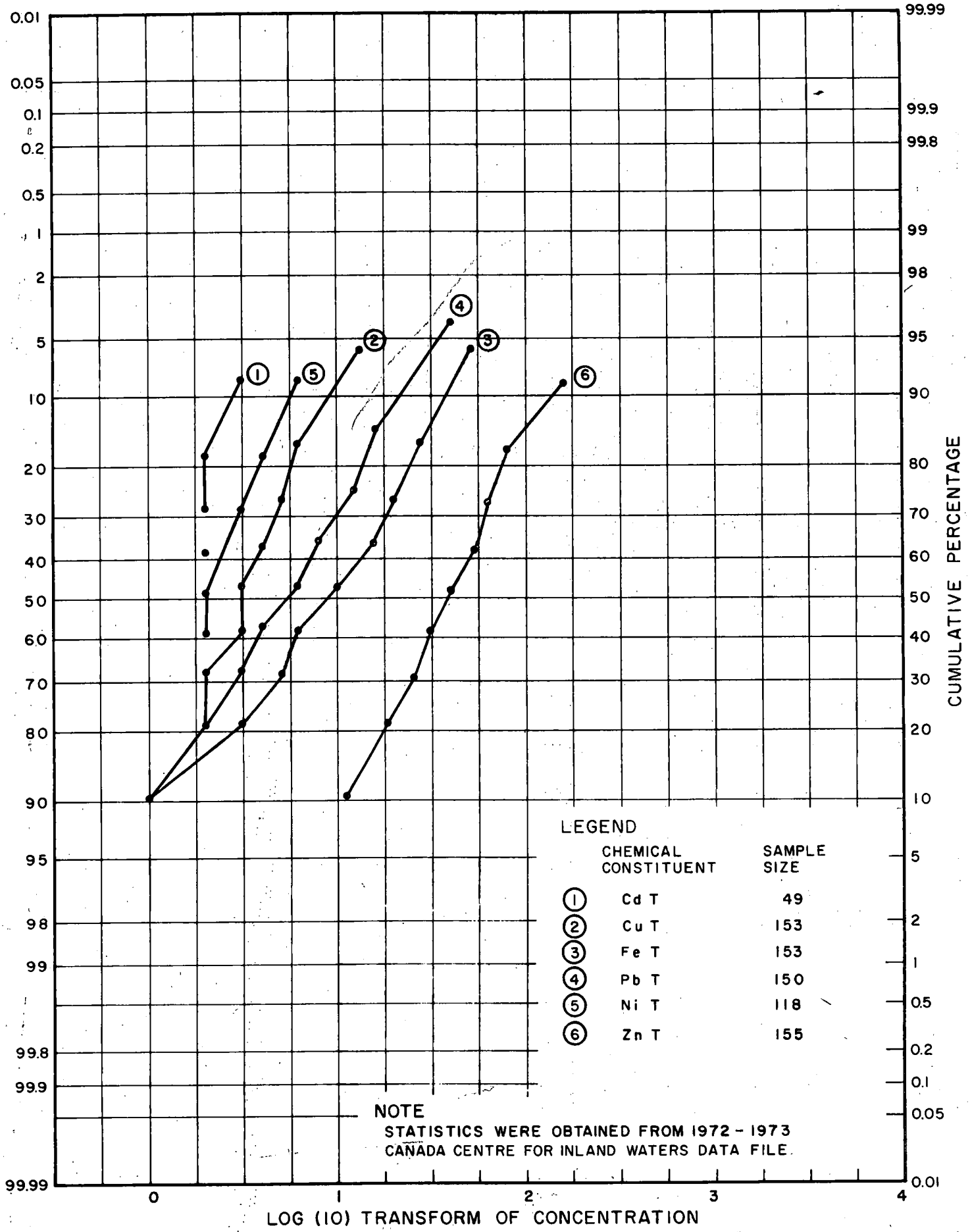


FIGURE 2 (f)

UPPER LAKES - CONCENTRATIONS

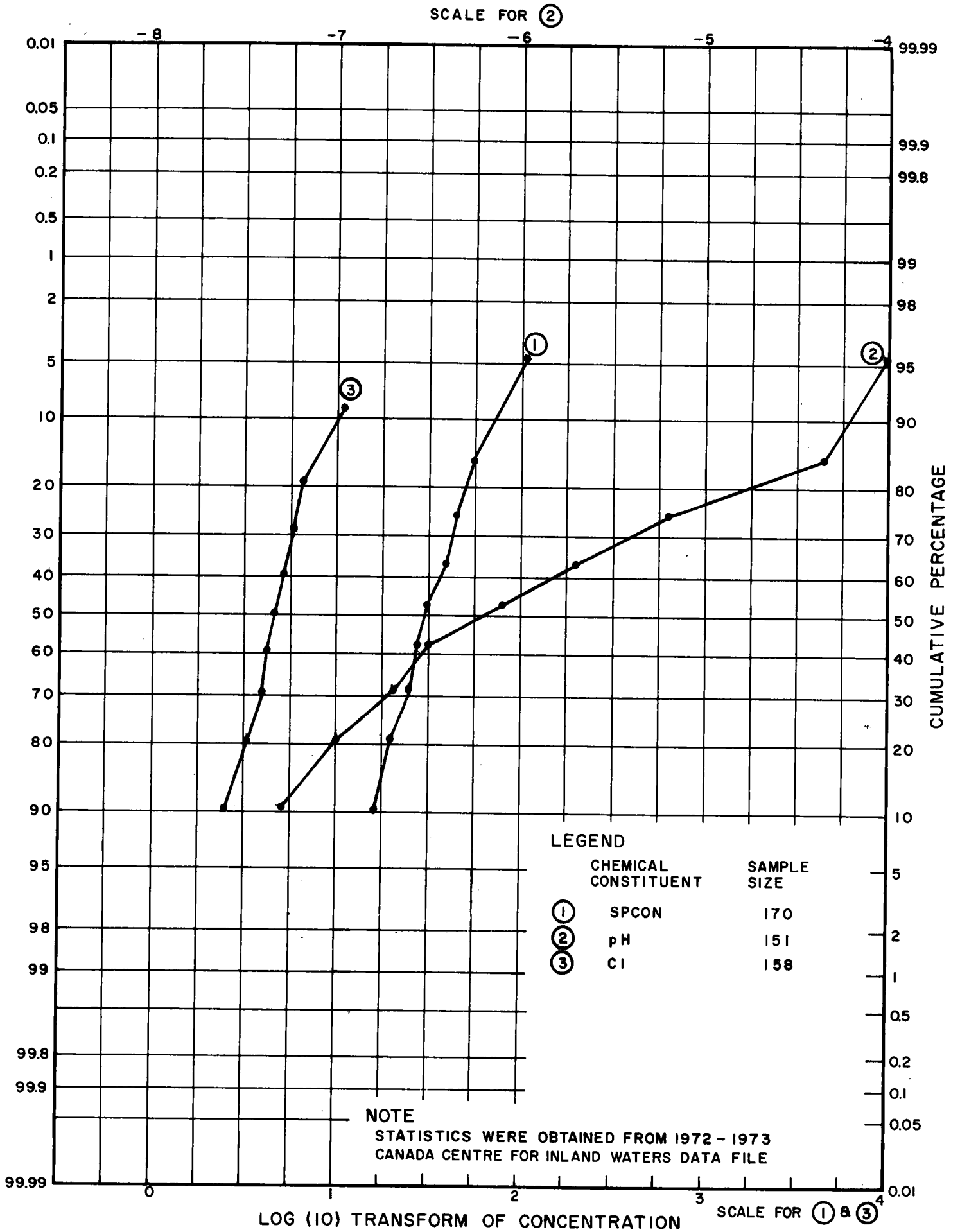


FIGURE 2 (g)

UPPER LAKES - CONCENTRATIONS

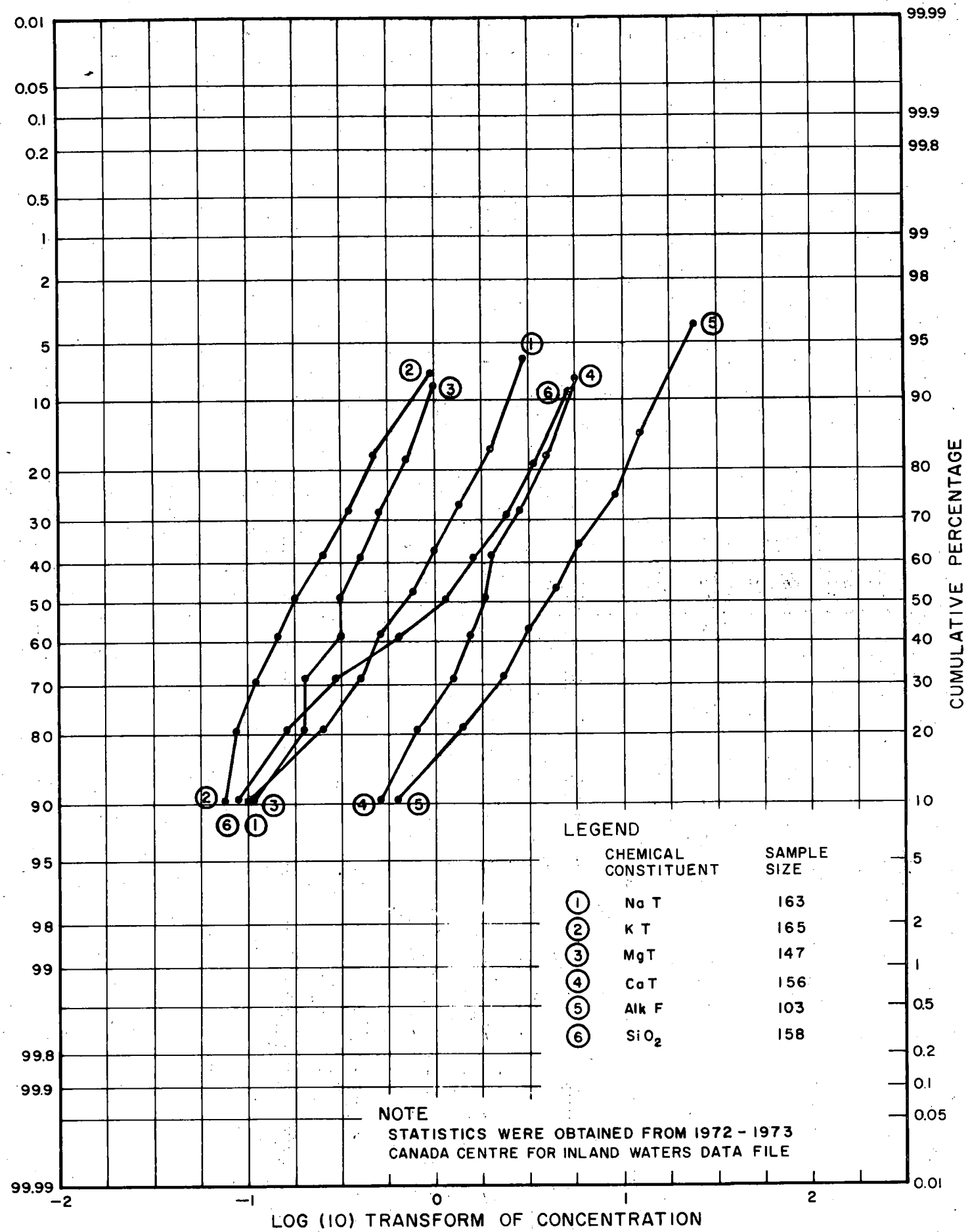


FIGURE 2 (h)

UPPER LAKES - CONCENTRATIONS

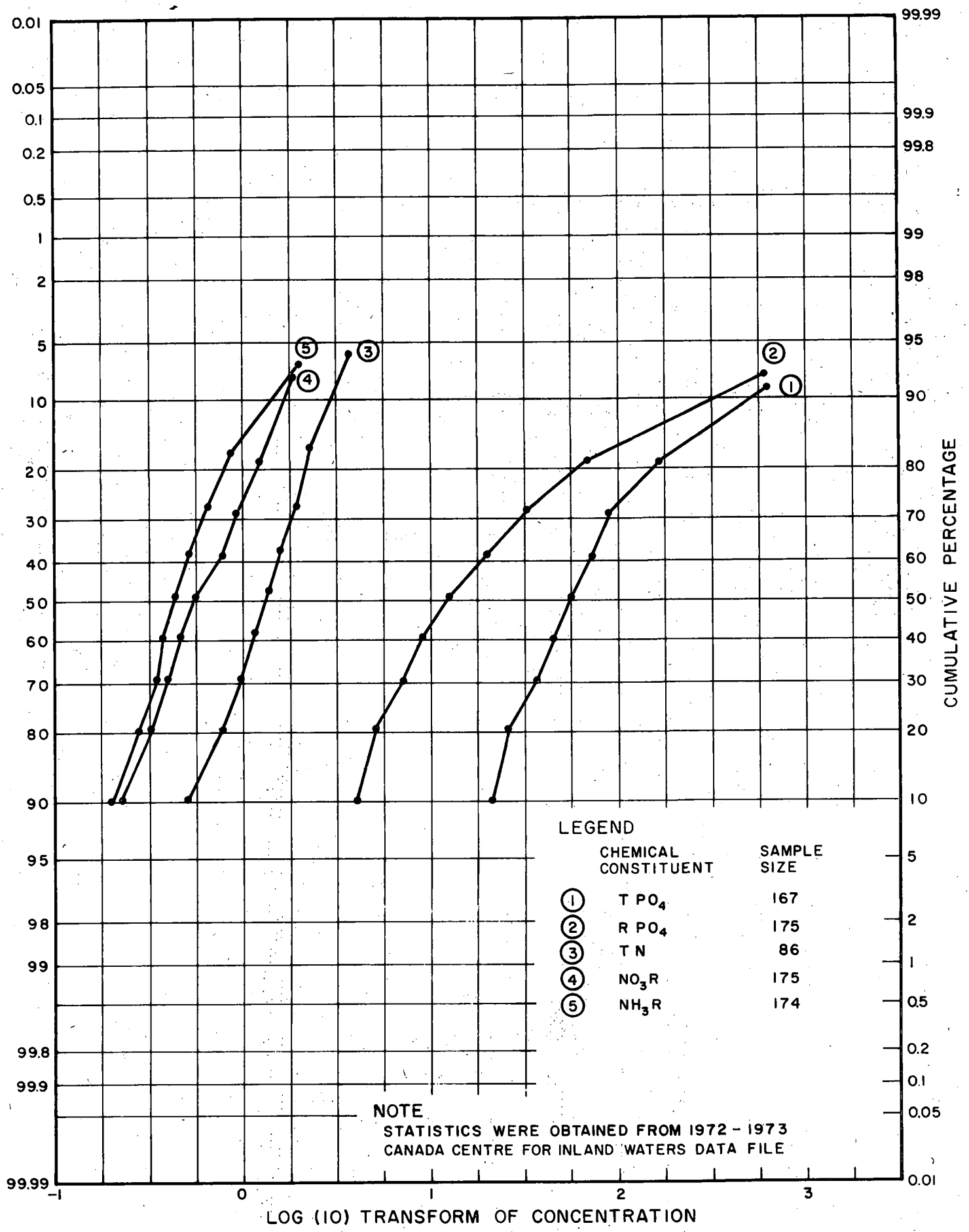


FIGURE 2 (i)

UPPER LAKES - CONCENTRATIONS

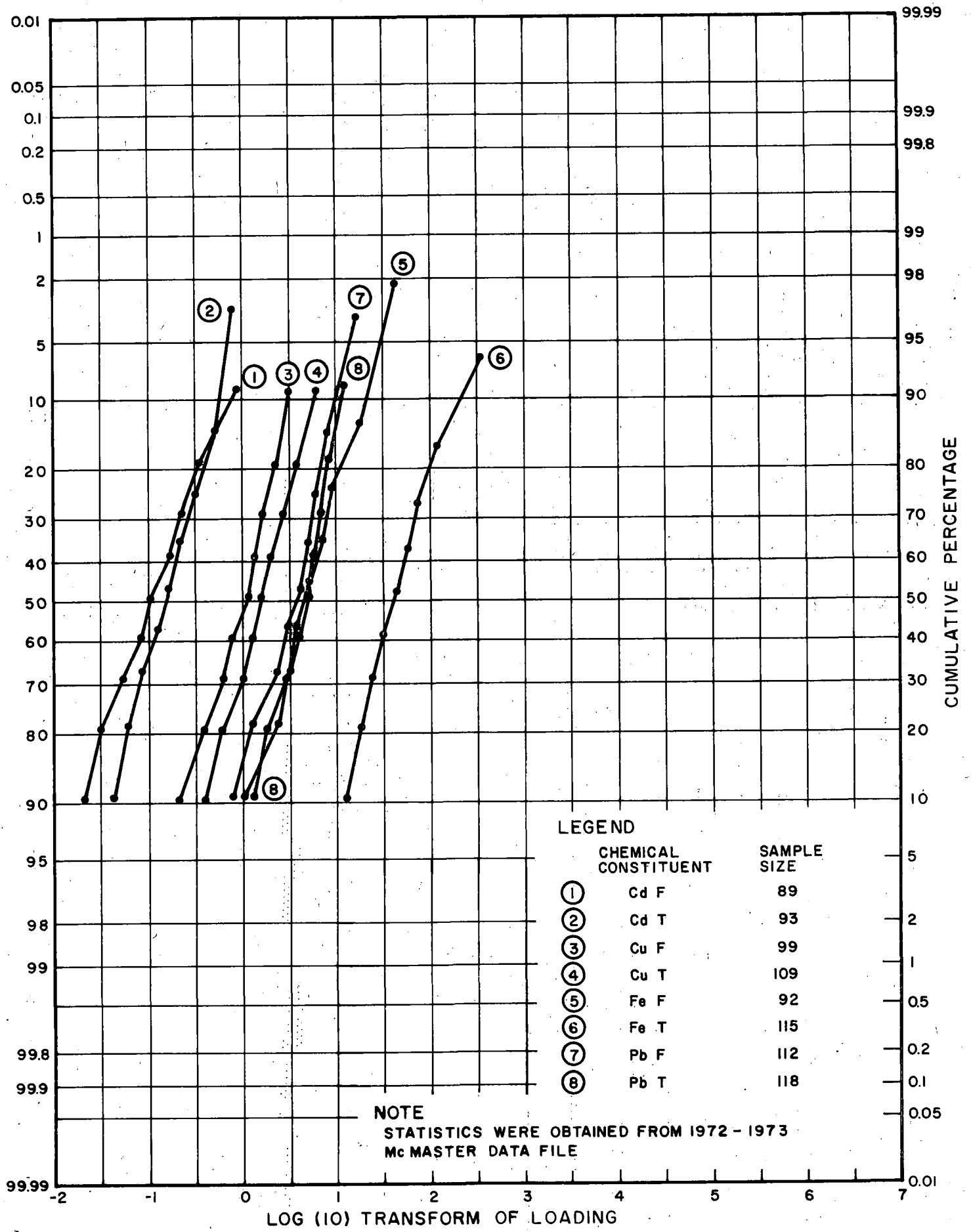


FIGURE 2 (j)

UPPER LAKES - LOADINGS

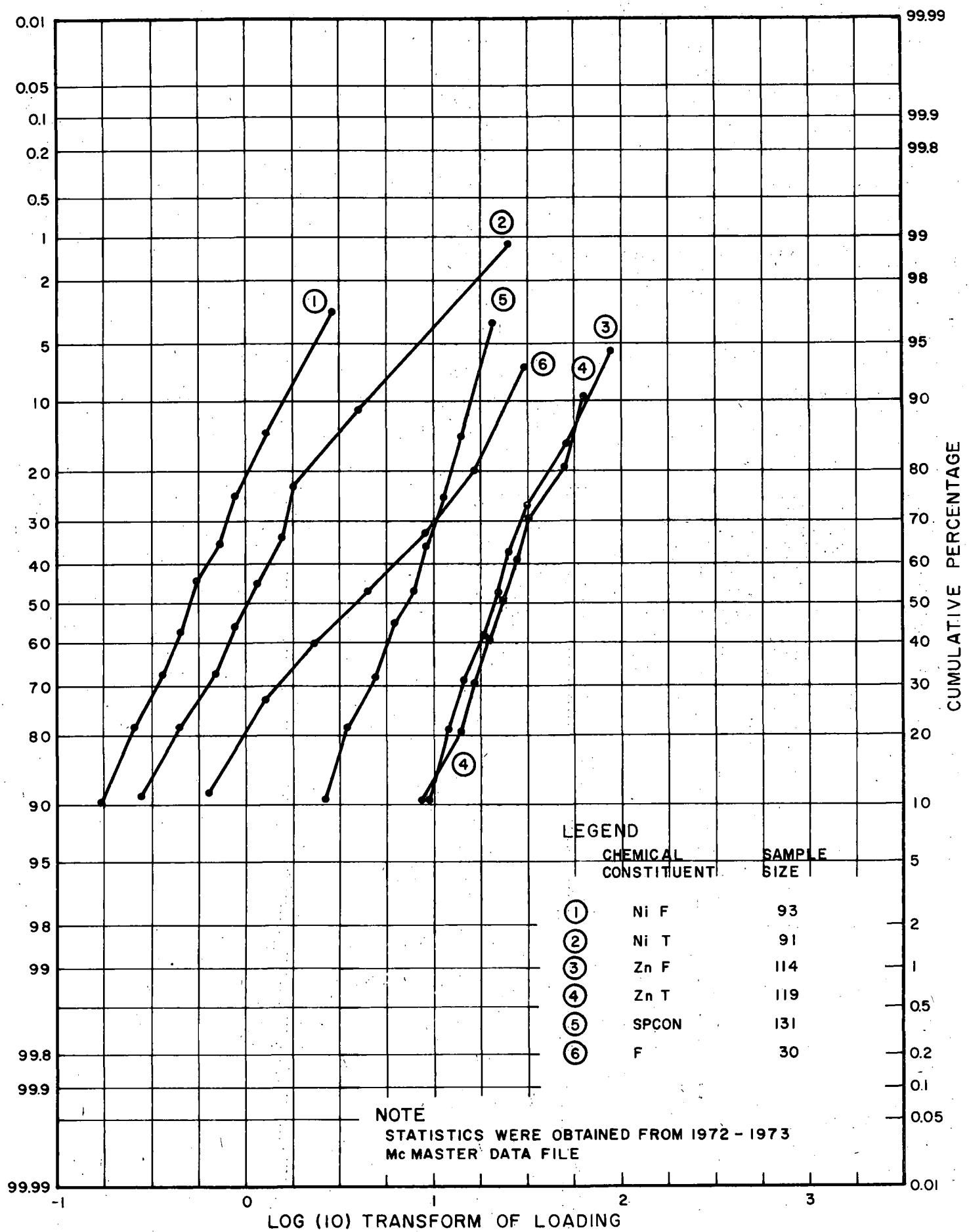


FIGURE 2 (k)

UPPER LAKES - LOADINGS

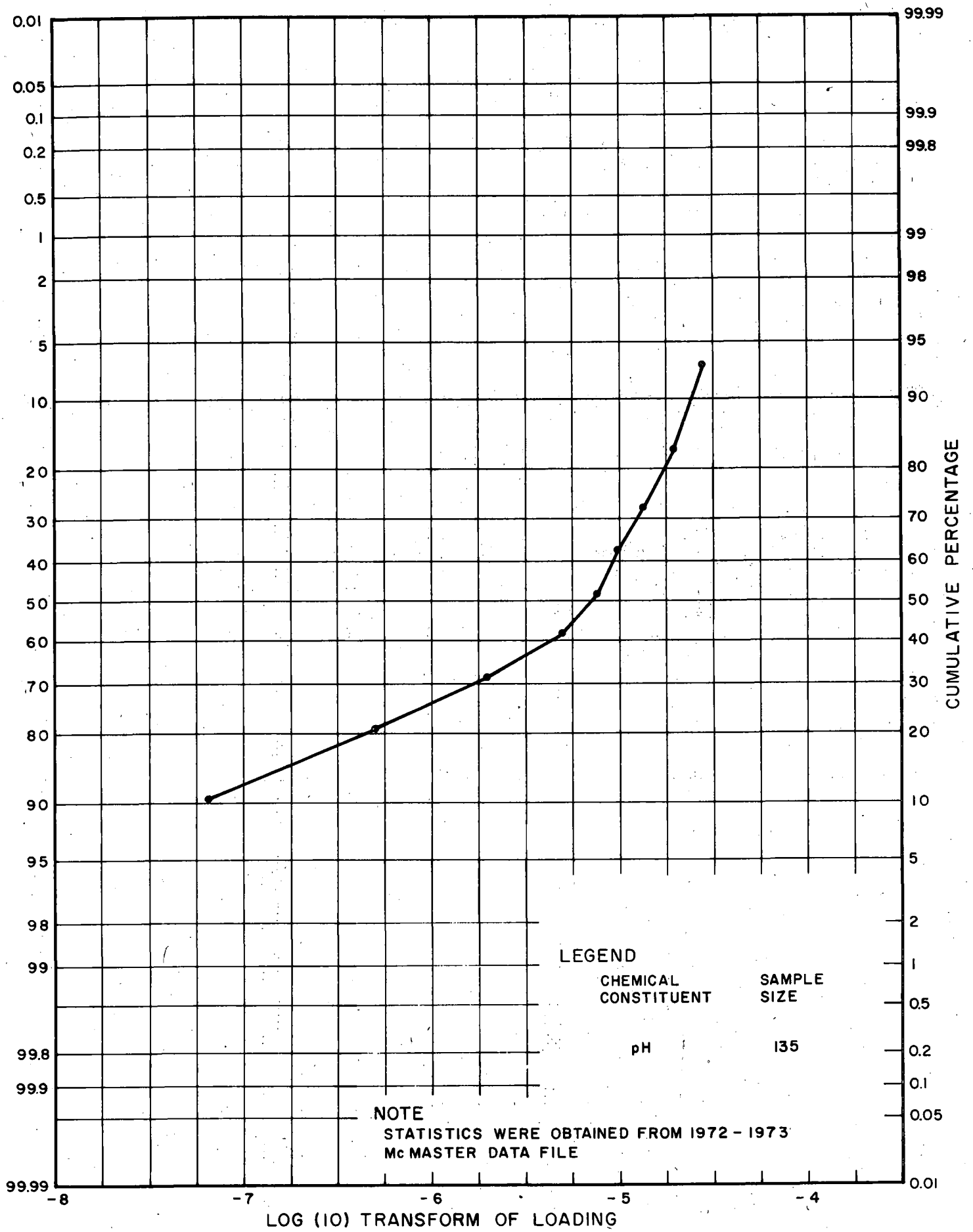


FIGURE 2 (1)

UPPER LAKES - LOADINGS

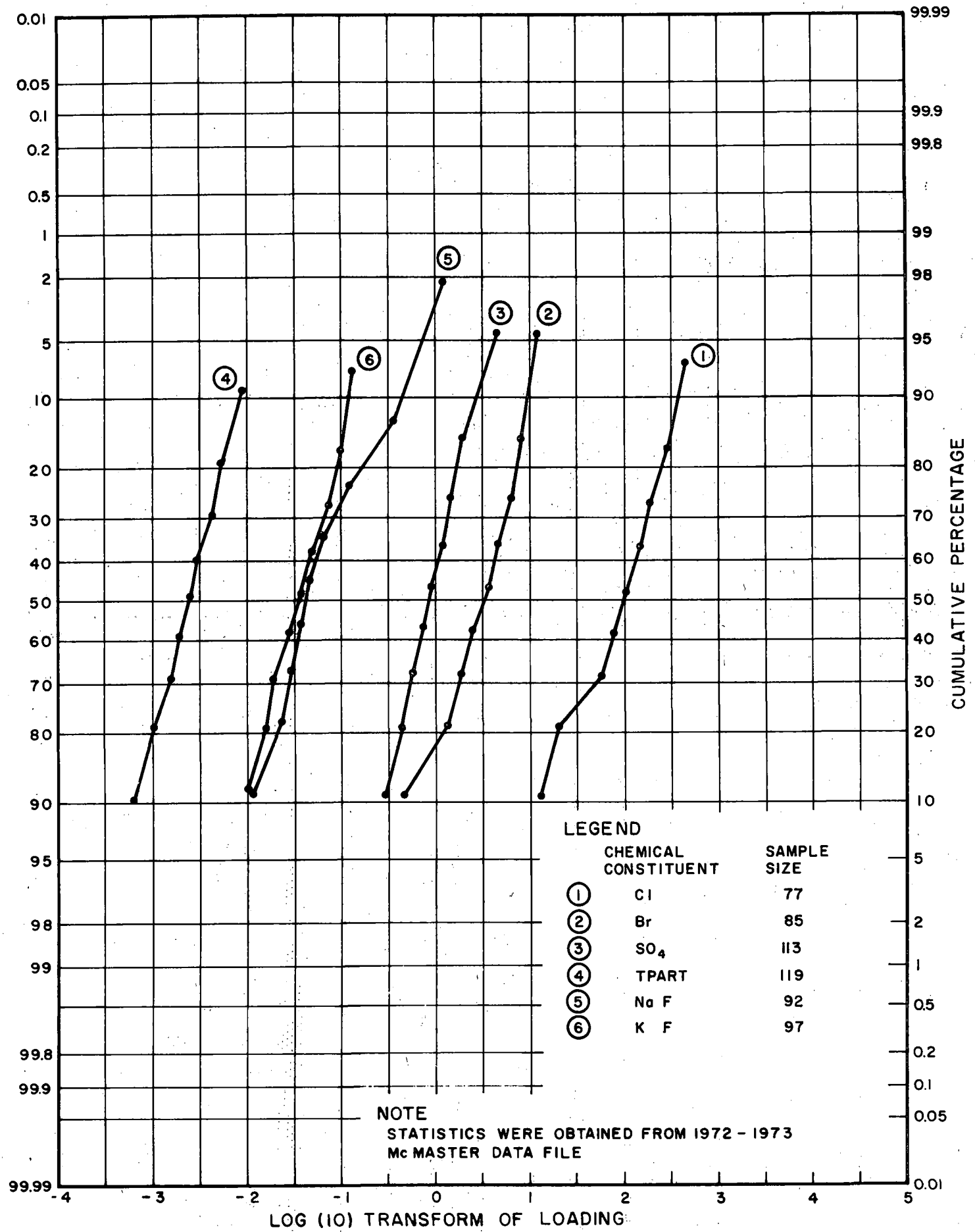


FIGURE 2 (m)

UPPER LAKES - LOADINGS

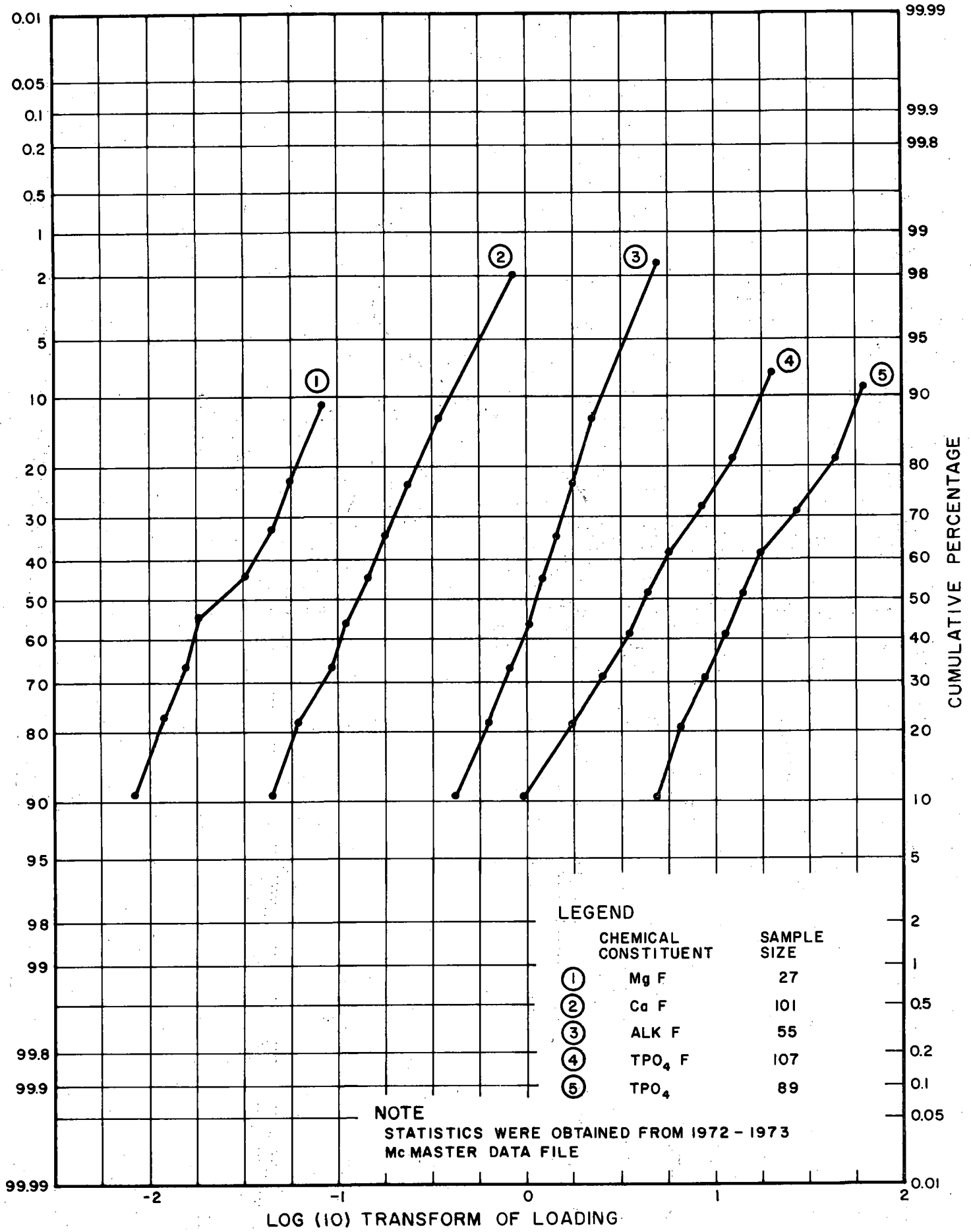


FIGURE 2 (n)

UPPER LAKES - LOADINGS

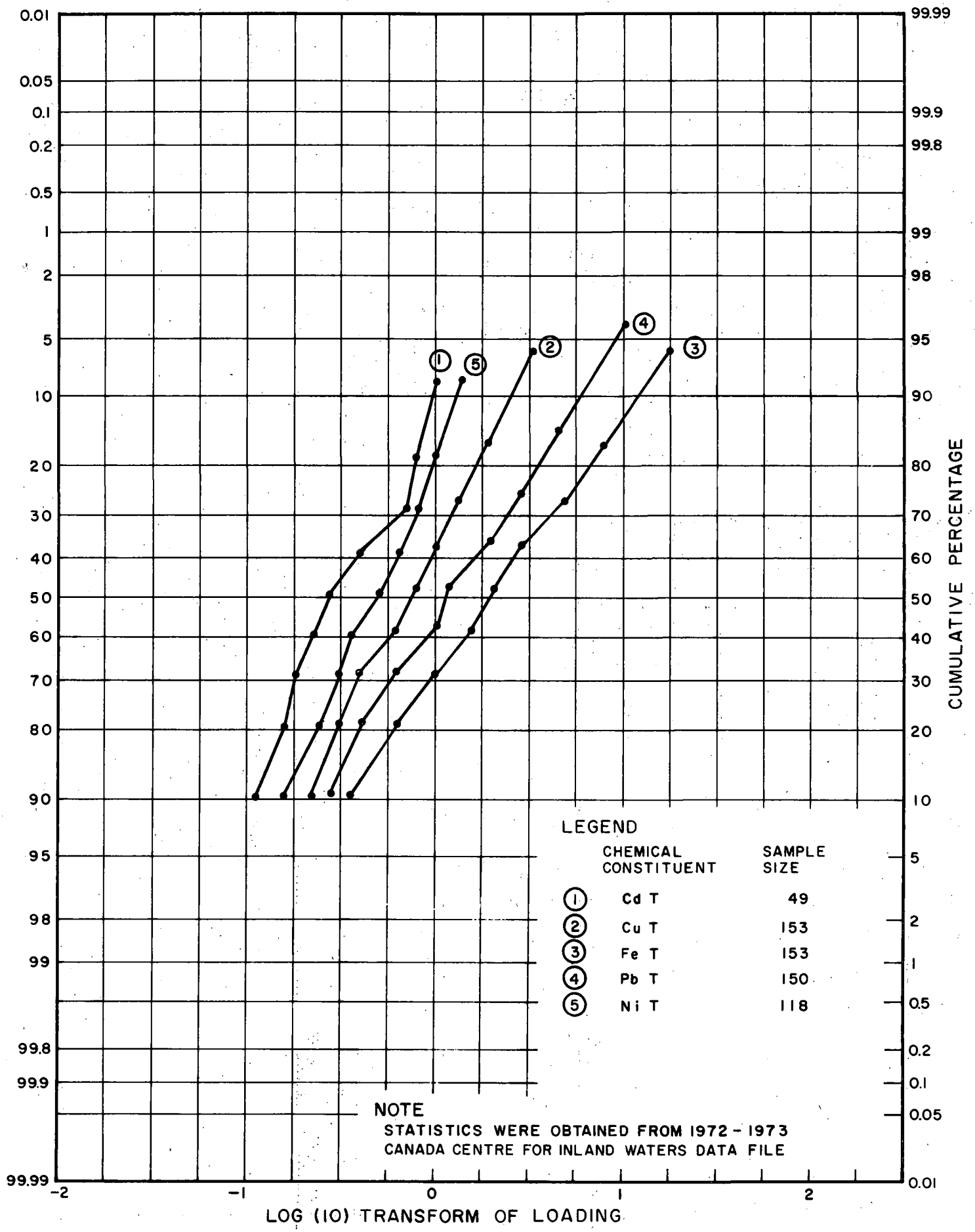


FIGURE 2 (o)

UPPER LAKES - LOADINGS

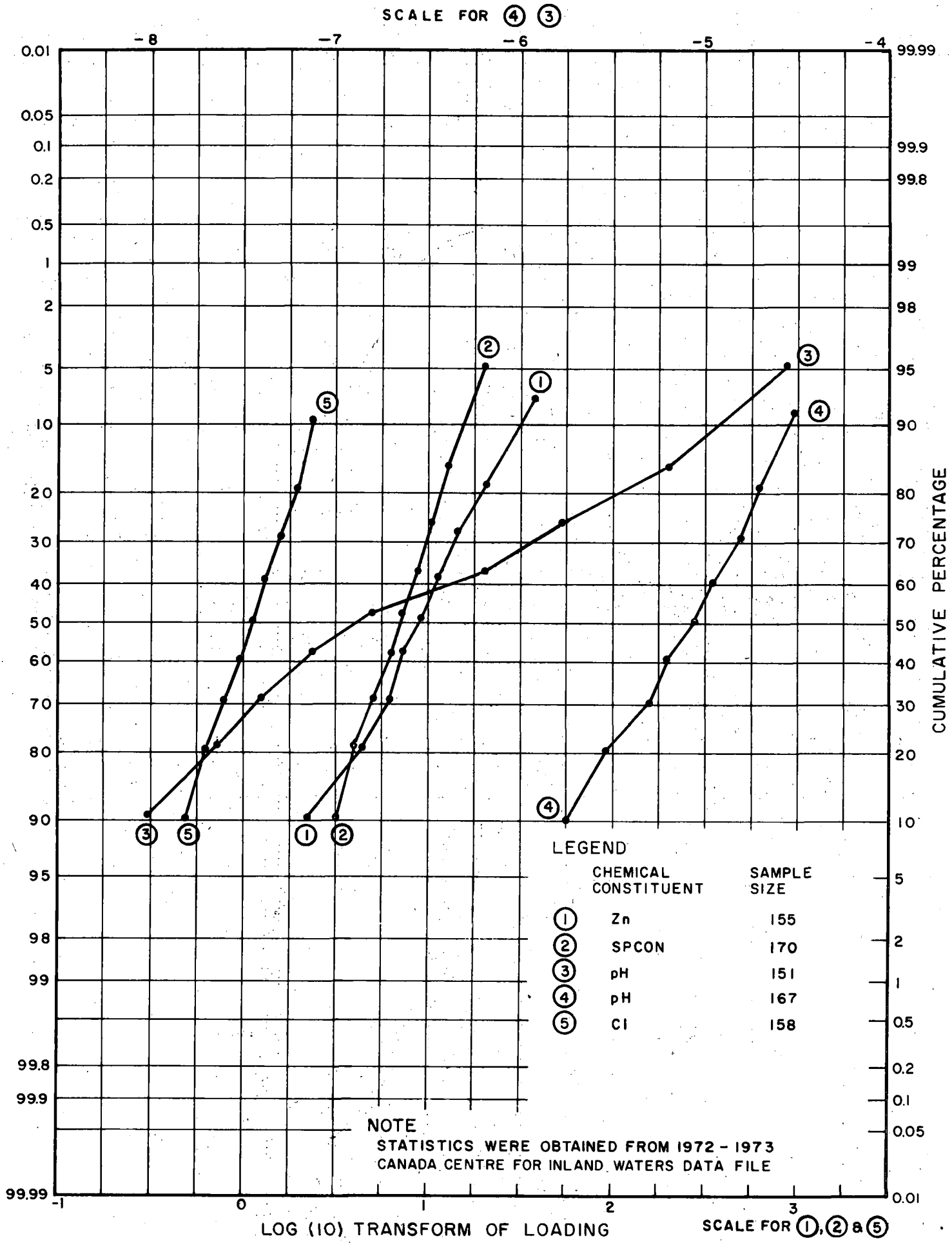


FIGURE 2 (p)

UPPER LAKES - LOADINGS

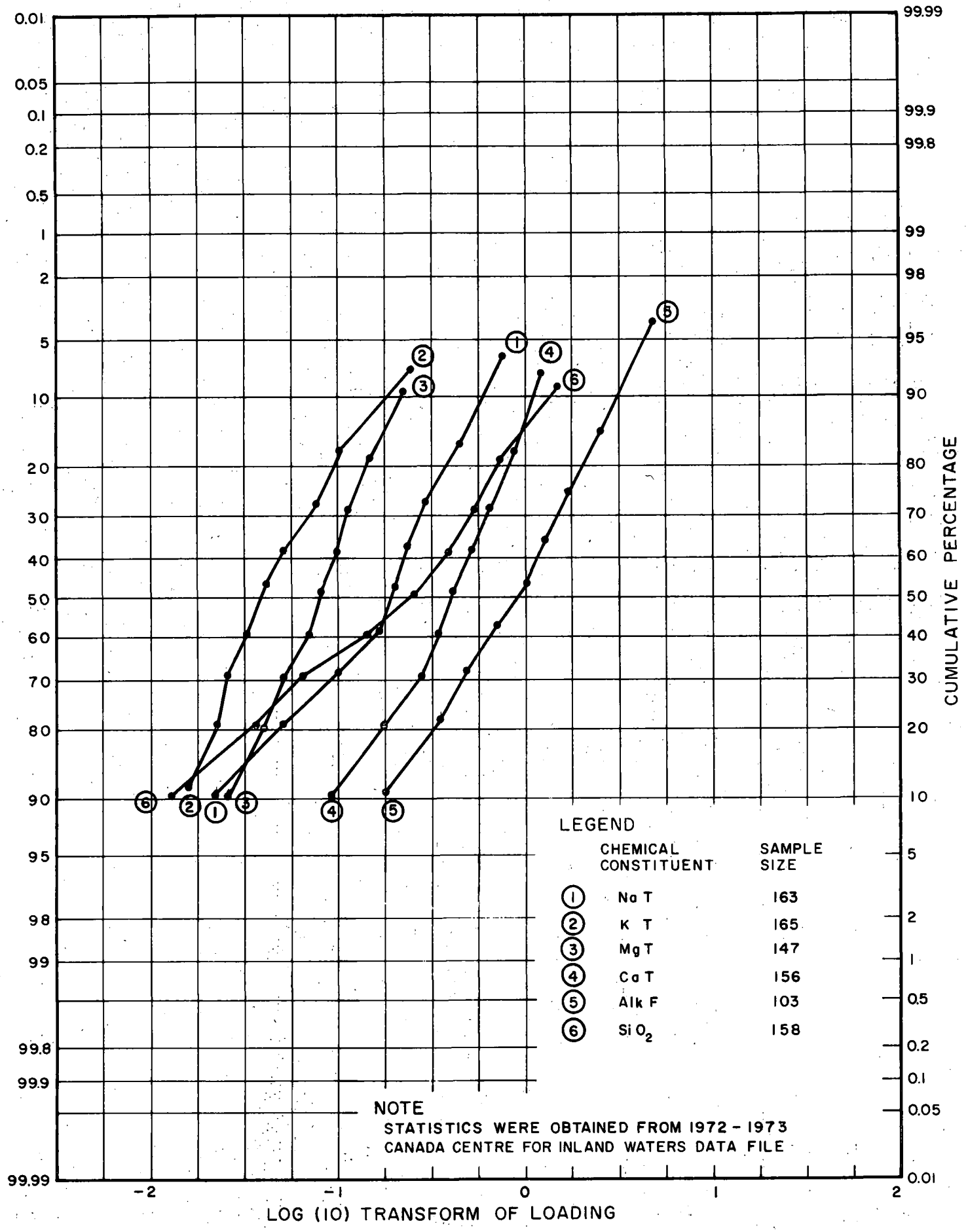


FIGURE 2 (q)

UPPER LAKES - LOADINGS

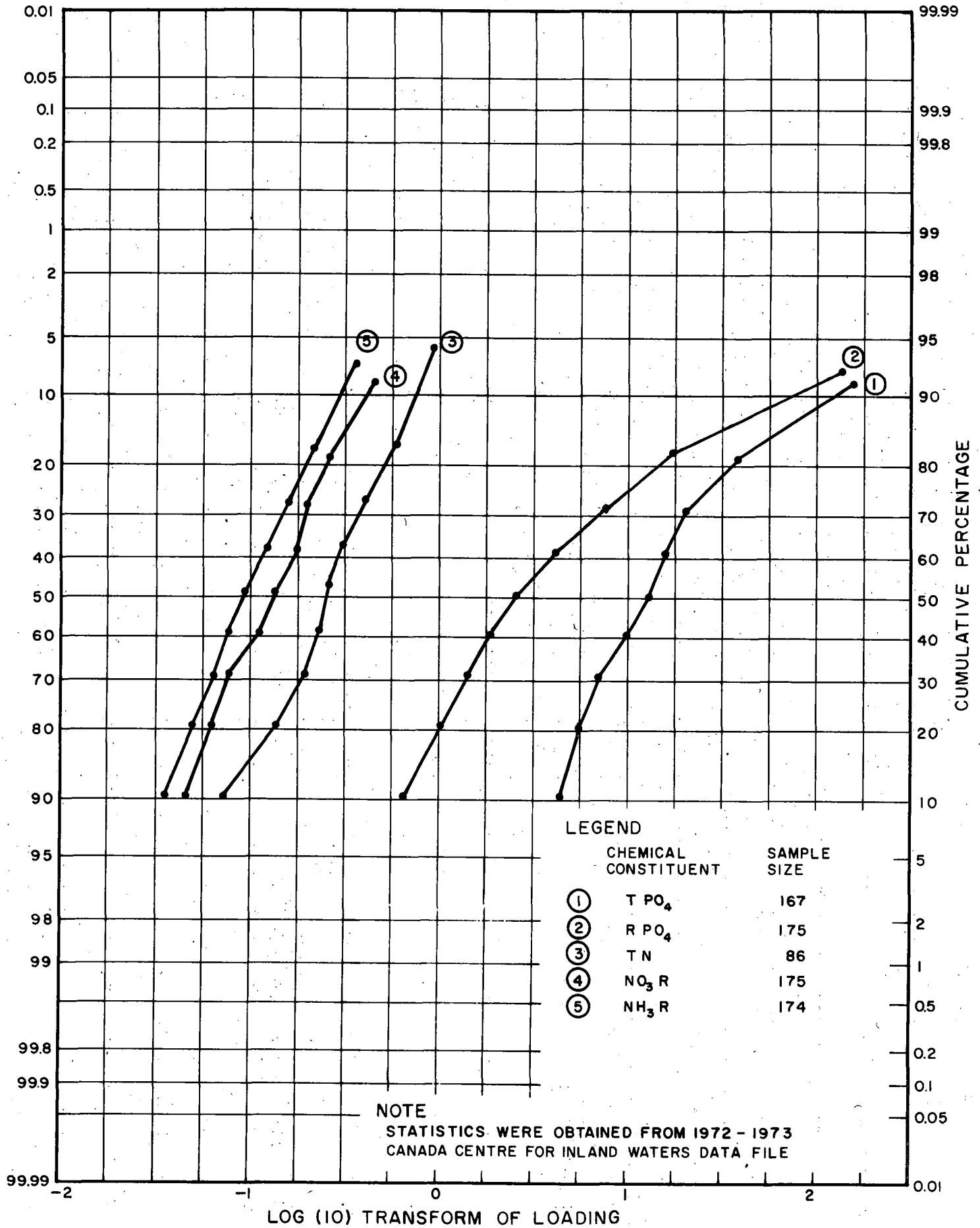


FIGURE 2 (r)

UPPER LAKES - LOADINGS

Interpretation

Data are lognormally distributed. Log transforms should be carried out on all data before carrying through statistical analysis requiring an assumption of the nature of the distribution.

3.2 - Monthly Data - Groupings of Parameters

Factor analysis was carried out on log transforms (with the exception of code 123-pH) in groups of 15 for all data. This analysis was carried out independently for the CCIW and McMaster monthly concentration and loading data. Many analyses were carried out in overlapping variable groupings in order to ascertain all possible patterns in the data. Both principal component analysis and varimax rotation were used with diagonals of the matrix equal to 1 and the criterion for inclusion of a factor was that the eigenvalue was greater than 0.9. Principal component analysis tends to load the first factor heavily, whereas varimax analysis tends to load factors evenly. This was the case in this analysis.

Grouping results into a few common factors was accomplished by noting associations occurring both in CCIW and McMaster data analysis and for different variable groupings. The following are the results of analysis with interpretation more or less in descending order of significance. ( ) suggest a weak correlation in the factor. All analyses were carried out on log-transformed data.

(1) Industrial: Cd, Cu, Fe, Pb, Zn, Particulate, SO_4, NO_3, (NH_3).

(2) Sudbury Smelter: Cu T, Ni T.

(3) (a) - Agriculture: PO_4-R, PO_4T, (NH_3).
(b) - Agriculture: Na, SO_4, NO_3, (K), (Mg), (Ca).

(4) Marine: Cl, Br.

(5) Lithology: Ca, pH.

(6) Automotive: (Pb F), (Br).

Factors (1) and (2) are common to both sets of data. So also is factor (4) except that Br is not measured in the CCIW data file; in this case, Cl comes out as a separate factor. Factor (3) often shows up as a phosphate-alkalinity association. Varimax analysis brought out the secondary factors, whereas principal component analysis defined factor (1) in all runs, generally lumped factor (2) in factor (1), and defined factor (4).

Interpretation

Factor analysis of CCIW-McMaster monthly concentration data shows a strong industrial factor defined by heavy metals, sulphate, and nitrate; a marine incursion factor defined by Cl and Br; a smelter factor defined by Cu and Ni; and an agricultural factor defined by various combinations of phosphorus, sulphate, nitrate, ammonia, and alkali-alkali metals. These groupings should be used to define analytical priorities and groupings for multivariate analysis.

3.3 - Monthly Samples - Comparison of Stations and Periods

Discriminant function analysis and Q-mode factor analysis are used on log (10) transformed data to define station grouping. This grouping is done first for all 23 stations; the stations are then regrouped and reanalyzed for time period. Variables considered for analysis are represented by the 6 factors determined in Section 2. This analysis is continuing.

3.4 - Monthly Samples - Comparison of CCIW-McMaster Data

Data have been collected independently for the past 2 years at Gore Bay, Ontario by McMaster and CCIW. Table 4 gives results by period for loading data. In interpreting the "error", there are certain subjective factors one must consider:

(a) NO_3 was analyzed after filtration for McMaster data. NO_3 was measured on the raw sample for CCIW data. One would expect CCIW to be greater than McMaster's-- it is by almost 10 times.

TABLE 4

COMPARISON OF LOADING DATA AT GORE BAY, ONTARIO, BETWEEN CCIW AND McMASTER FOR SELECTED CODES - Units are $g/cm^2/day$ - CCIW (C), McMaster (M), Rain(R), Snow(S) - Code Numbers and Acronyms are Shown

Period Began Month and Year	240-T P $\times 10^{-9}$	237-NO_3 F(M) 243-NO_3 R(C) $\times 10^{-6}$	116-Ni T $\times 10^{-9}$	113-Pb T $\times 10^{-9}$	107-Cu T $\times 10^{-9}$	232-ALKF $\times 10^{-6}$	127-SO_4 $\times 10^{-6}$	Sampler Type
01-72C	28.4	1.53	-	-	-	-	-	R
M		-	-	-	-	-	-	S
02-72C	13.0	0.85	1.1	1.8	2.1	0.23	2.4	R
M	-	0.07	-	-	-	-	<0.46	S
03-72C	14.0	0.53	3.5	6.3	3.5	-	1.8	R
M	-	0.05	-	-	-	-	0.86	S
04-72C	7.4	0.44	1.4	1.4	1.2	-	0.86	R
M	-	-	1.6	2.4	<3.0	-	0.80	S
05-72C	4.6	0.17	0.6	-	0.18	0.73	1.0	R
M	-	-	-	3.9	1.2	-	0.81	S
06-72C	33.0	0.14	-	0.52	0.59	0.36	0.89	R
M	-	-	-	0.4	0.40	-	-	S
07-72C	14.0	0.13	-	2.0	0.50	2.8	1.3	R
M	-	-	-	-	-	-	0.06	S
08-72C	10.0	0.08	0.6	0.3	0.32	0.97	1.7	R
M	-	-	-	-	2.5	-	1.2	S
09-72C	8.4	0.19	-	1.4	1.4	0.14	1.4	R
M	-	-	1.8	3.0	1.6	-	-	S

Table 4 (Cont'd)

Period Began Month and Year	240-T P x 10^{-9}	237-NO_3 F(M) 243-NO_3 R(C) x 10^{-6}	116-Ni T x 10^{-9}	113-Pb T x 10^{-9}	107-Cu T x 10^{-9}	232-ALKF x 10^{-6}	127-SO_4 x 10^{-6}	Sampler Type
10-72C	3.4	0.11	-	-	-	0.41	0.85	R
M	9.0	-	0.2	4.3	2.8	-	0.69	S
11-72C	-	0.15	-	0.3	0.34	0.34	0.76	R
M	-	-	5.4	6.9	12.0	-	-	S
12-72C	12.0	0.21	-	9.6	1.8	-	0.93	S
M	3.2	-	1.0	5.0	0.57	-	0.45	S
01-73C	11.0	0.14	0.2	-	0.63	0.54	0.5	S
M	23.0	-	4.1	1.3	1.7	-	1.4	S
02-73C	5.6	0.12	0.1	0.1	0.6	-	0.50	S
M	19.0	-	1.6	6.1	2.4	-	0.37	S
03-73C	7.2	0.20	1.9	6.3	1.1	-	-	S
M	4.3	-	1.5	4.9	1.7	-	0.22	S
04-73C	6.7	0.26	0.6	2.6	0.81	-	1.5	R
M	-	-	-	-	-	-	-	S
05-73C	5.3	0.12	1.5	2.7	1.9	0.11	1.0	R
M	44.0	-	1.7	9.6	<0.85	<0.04	2.1	S
06-73C	20.0	2.7	1.1	0.6	1.1	4.6	1.6	R
M	39.0	-	3.1	3.3	0.11	0.67	1.4	S
07-73C	26.0	0.08	0.1	0.1	0.25	0.24	0.65	R
M	41.0	-	0.5	2.8	9.0	0.26	0.2	S
08-73C	319.0	0.22	0.7	0.3	0.66	1.7	2.1	R
M	57.0	-	0.2	8.6	<0.26	4.1	1.7	S
09-73C	6.2	0.08	0.1	0.3	0.30	0.41	0.80	R
M	14.0	-	0.3	1.1	0.43	0.53	0.28	S

Table 4 (Cont'd)

Period Began Month and Year	240-T P x 10^{-9}	237-NO_3 F(M) 243-NO_3 R(C) x 10^{-6}	116-Ni T x 10^{-9}	113-Pb T x 10^{-9}	107-Cu T x 10^{-9}	232-ALKF x 10^{-6}	127-SO_4 x 10^{-6}	Sampler Type
10-73C	5.5	0.14	0.3	2.6	0.57	-	1.3	R
M	12.0	-	1.2	1.6	0.09	1.1	0.79	S
11-73C	28.0	0.28	1.0	9.8	3.3	-	2.4	R
M	9.0	-	1.2	1.3	0.92	0.88	-	S

(b) For Ni T, Pb T, Cu T: McMaster data represent a sample doubly digested in acid to near dryness. For CCIW data, the results are for "reactive" metal. One would expect McMaster results to be higher than CCIW results. This is generally the case with exceptions.

(c) McMaster data are for a snow-type sampler in all cases. CCIW results are for a combination of snow and rain samplers. One would expect differences for the different samplers, particularly in winter months as the rain sampler is heated and without an Alter Shield.

Due to the gaps in data it is impossible to do a multivariate "analysis of variance". Table 5 is one summary of comparison of the two sets of analyses.

Interpretation of results by parameter are:

(a) Total phosphate: the reproducibility is about 180 per cent with three notable exceptions. These exceptions show CCIW data to be very high (although both sets of data are above the normal) and represent different samplers during winter period (except for 1). Excluding these three extremes, the difference is about 60 per cent. With these two exceptions, the McMaster loading data always measure high compared to the CCIW data. This can be explained by lack of collection efficiency of the CCIW rain type samplers.

(b) The difference between NO_3 F and NO_3 R is about 10 times. The difference is interpreted as being primarily due to a filtered versus a non-filtered sample.

(c) Ni, Pb, and Cu show a deviation of 100, 180, and 300 per cent respectively. McMaster data are consistently greater than CCIW data. This is due to difference in analytical design and sampler collection efficiency.

(d) Alkalinity shows a 250 per cent difference with one sample difference of 590 per cent. Ignoring this one analysis, the difference is 100 per cent. This may be due to difference in sampler design.

(e) SO_4 shows a 550 per cent difference with three notable exceptions. Ignoring these extremes, the difference is about 50 per cent. For this variable, the CCIW data are generally greater than the McMaster data, suggesting an analytical design difference (McMaster data are filtered) or a lack of analytical reproducibility.

TABLE 5

RESULTS OF REPRODUCIBILITY STUDY -
Data in Table Represent $(x_C - x_M)/x_M$ Where x_C and x_M are Loading Data of CCIW and McMaster Respectively

Period Began Month and Year	240-T P $\times 10^{-9}$	237-NO_3F(M) 243-NO_3R(C) $\times 10^{-6}$	116-Ni T $\times 10^{-9}$	113-Pb T $\times 10^{-9}$	107-Cu T $\times 10^{-9}$	232-ALKF $\times 10^{-6}$	127-SO_4 $\times 10^{-6}$	Sampler Type C/M
01-72	-	-	-	-	-	-	-	-
02-72	-	11.0	-	-	-	-	-	R/S
03-72	-	9.6	-	-	-	-	1.1	R/S
04-72	-	-	-0.13	-0.42	-	-	0.08	R/S
05-72	-	-	-	-1.0	-0.85	-	0.23	R/S
06-72	-	-	-	0.3	0.48	-	-	R/S
07-72	-	-	-	-	-	-	21.0	R/S
08-72	-	-	-	-	-0.88	-	0.42	R/S
09-72	-	-	-1.0	-0.53	-0.13	-	-	R/S
10-72	-0.62	-	-	-	-	-	0.23	R/S
11-72	-	-	-1.0	-0.96	-0.97	-	-	R/S
12-72	2.8	-	-1.0	0.92	2.2	-	1.1	S/S
01-73	-0.02	-	-0.95	-1.0	-0.63	-	-0.64	S/S
02-73	-0.71	-	-0.14	-0.98	-0.75	-	0.35	S/S
03-73	0.67	-	0.27	0.29	-0.35	-	-	S/S
04-73	-	-	-	-	-	-	-	R/S
05-73	-0.88	-	-0.12	-0.72	-	-	-0.52	R/S
06-73	-0.49	-	-1.6	-0.82	9.0	5.9	0.14	R/S
07-73	-0.37	-	-0.8	-0.96	-0.97	-0.18	2.3	R/S
08-73	4.6	-	2.5	-0.97	-	-0.59	0.24	R/S
09-73	-0.56	-	-0.67	-0.73	-0.30	-0.23	1.9	R/S
10-73	-0.54	-	-0.75	0.63	5.3	-1.0	0.65	R/S
11-73	2.1	-	-0.17	6.5	2.6	-	-	R/S
$\left[\Sigma\left(\frac{\Delta x}{x}\right)^2/n\right]^{1/2}$	1.8	10.0	1.0	1.8	3.0	2.5	5.5	-
NO.M>C	8	0	12	12	9	5	2	-
NO.C>M	4	2	2	4	5	1	13	-

Interpretation:

(a) For the identical parameter, loading data are reproducible to within about 50 per cent. A few notable exceptions exist, suggesting contamination. This reproducibility also includes the effect of different sampler design.

(b) The heated rain sampler design of CCIW is less efficient than the Alter Shield snow collector of McMaster.

(c) The exact sample preparation, especially with regard to filtering, effects differences of up to 1,000 per cent.

3.5 - Monthly Samples - Loading Data

The arithmetic mean of monthly loading data was calculated for T PO_4, NO_3R - NO_3 F, SiO_2, Alk, T Cu, T Pb, T Ni, T Zn, and SO_4; contour maps of loading were constructed and are shown in Figures 3(a) to 3(i). Isolated extreme values are circled but were not considered in construction of the contours.

The following is a list of apparently abnormal data reflecting a local source:

T PO_4	Station 130, 131 Caribou Island, Cooper Harbor Insects. Fall values approach normal. Station 25, 137 Shawanaga, Kilbear Park. Possibly CIL explosives plant at Nobel.
NO_3R	Station 137 Kilbear Park. Possibly CIL explosives plant at Nobel.
SiO_2	Station 137 Possibly Kilbear Park.
Ni T	Station 3 Killarney. Possibly Sudbury smelter. If so, contours must be changed. Station 111 Possibly Schreiber.
SO_4	Station 137 Kilbear Park and possibly CIL explosives plant.

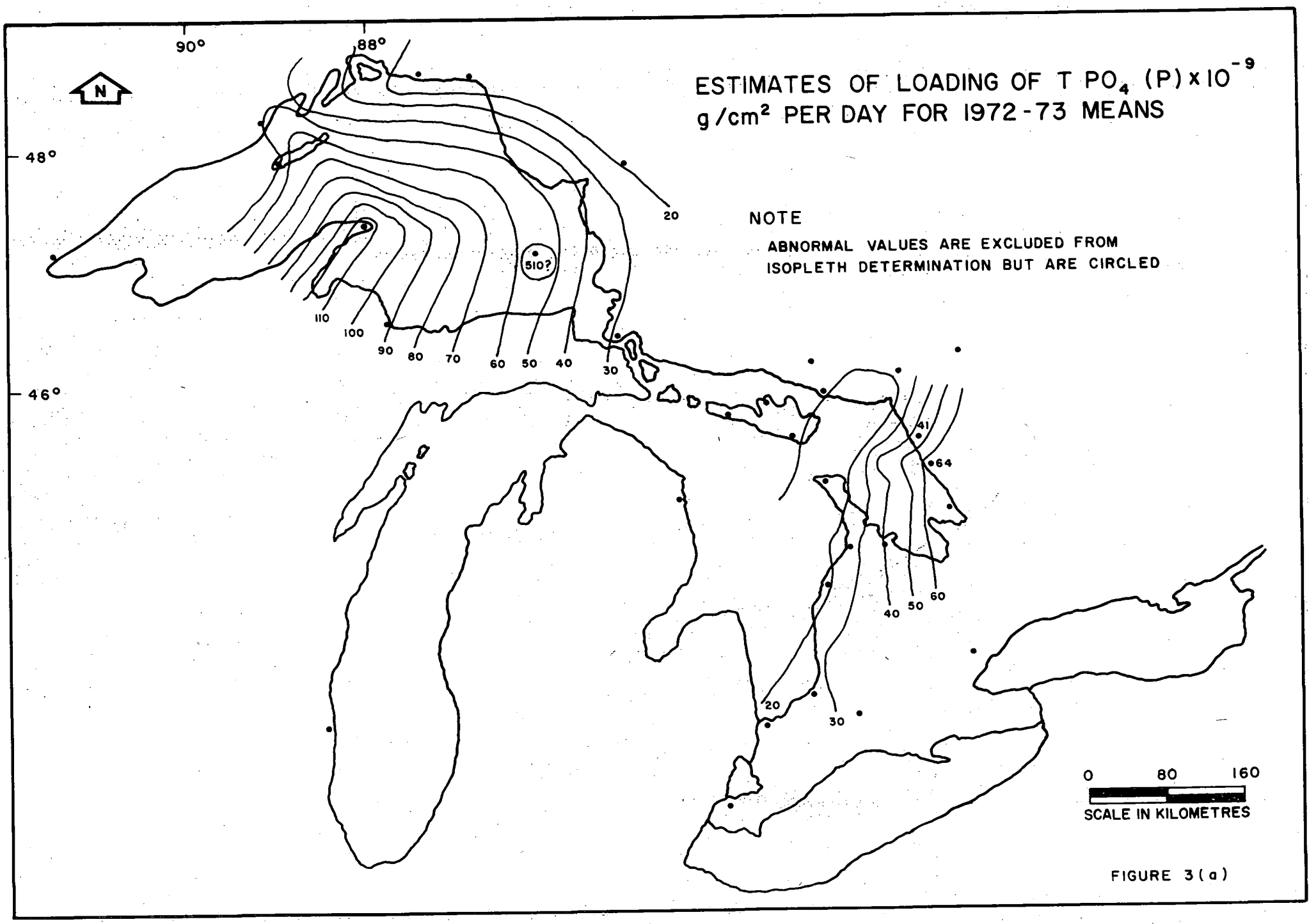

ESTIMATES OF LOADING OF T PO_4 (P) x 10^{-9}
g/cm² PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
110
100
90
80
70
60
50
40
30
20
510?
41
64
40
50
60
20
30
0
80
160
SCALE IN KILOMETRES

FIGURE 3(a)

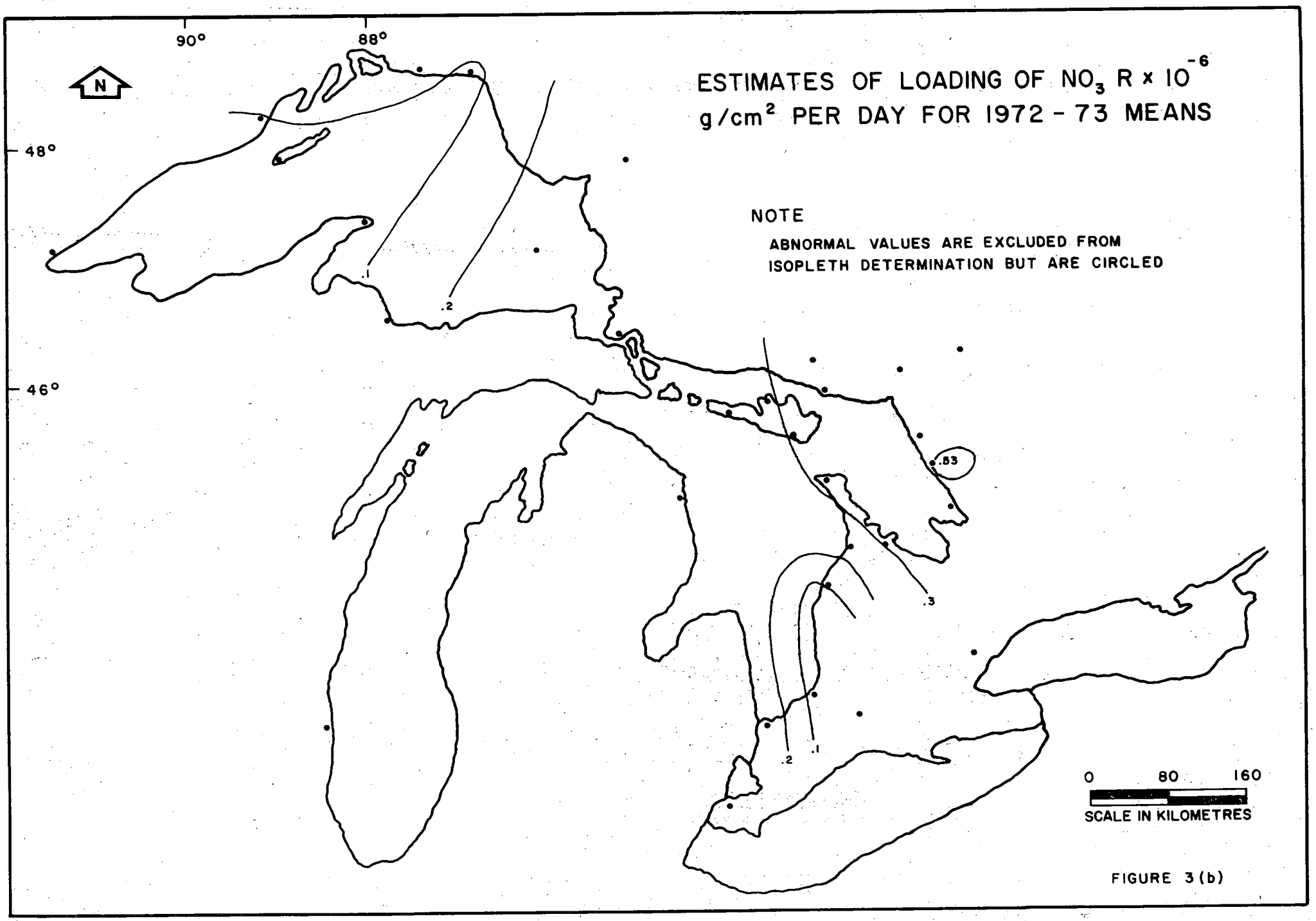

ESTIMATES OF LOADING OF NO_3 R x 10^{-6}
g/cm² PER DAY FOR 1972 - 73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
.1
.2
.53
.3
.2
.1
0
80
160
SCALE IN KILOMETRES

FIGURE 3(b)

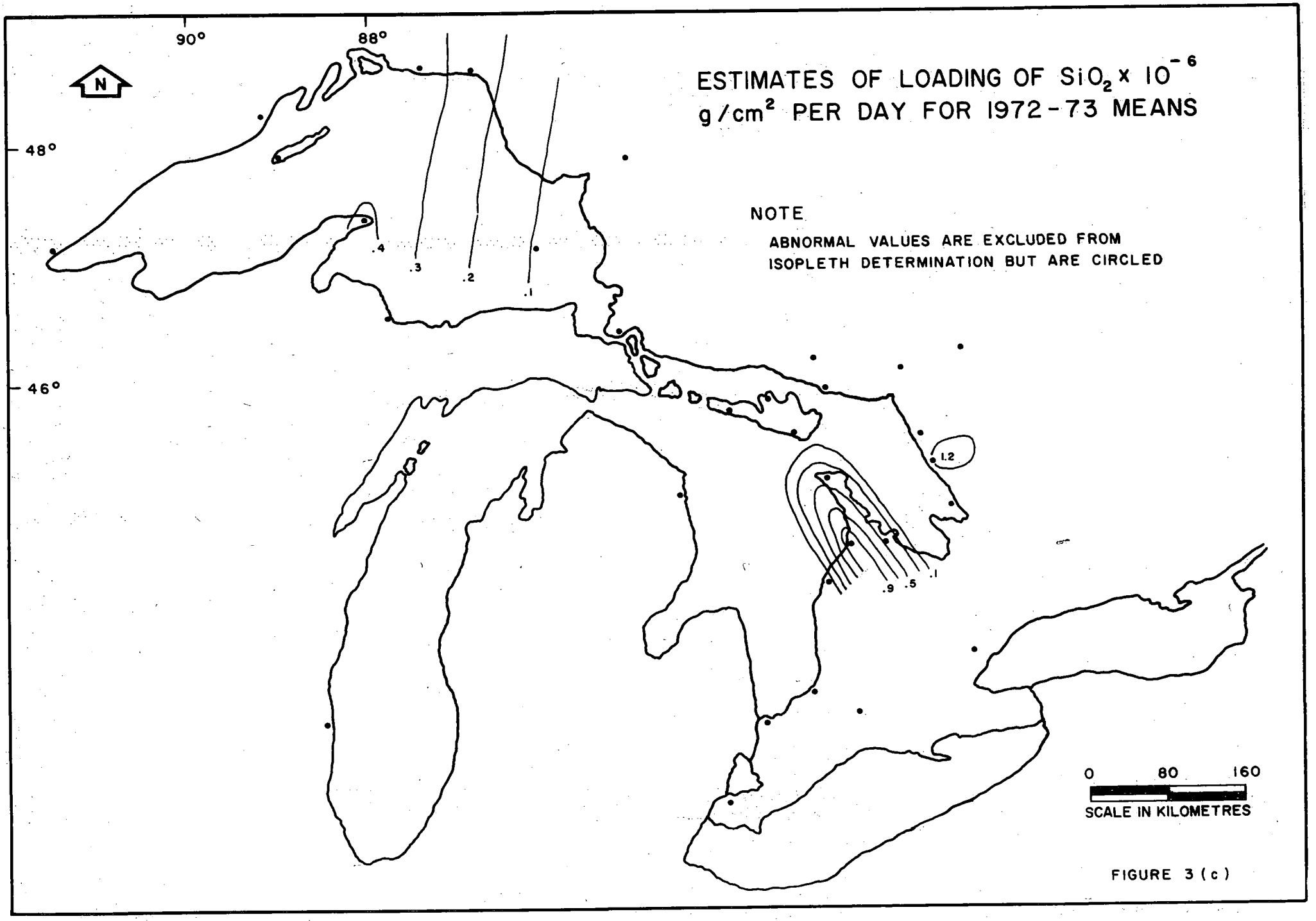

ESTIMATES OF LOADING OF $SiO_2 \times 10^{-6}$ g/cm² PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
.4
.3
.2
.1
1.2
.9
.5
.1
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (c)

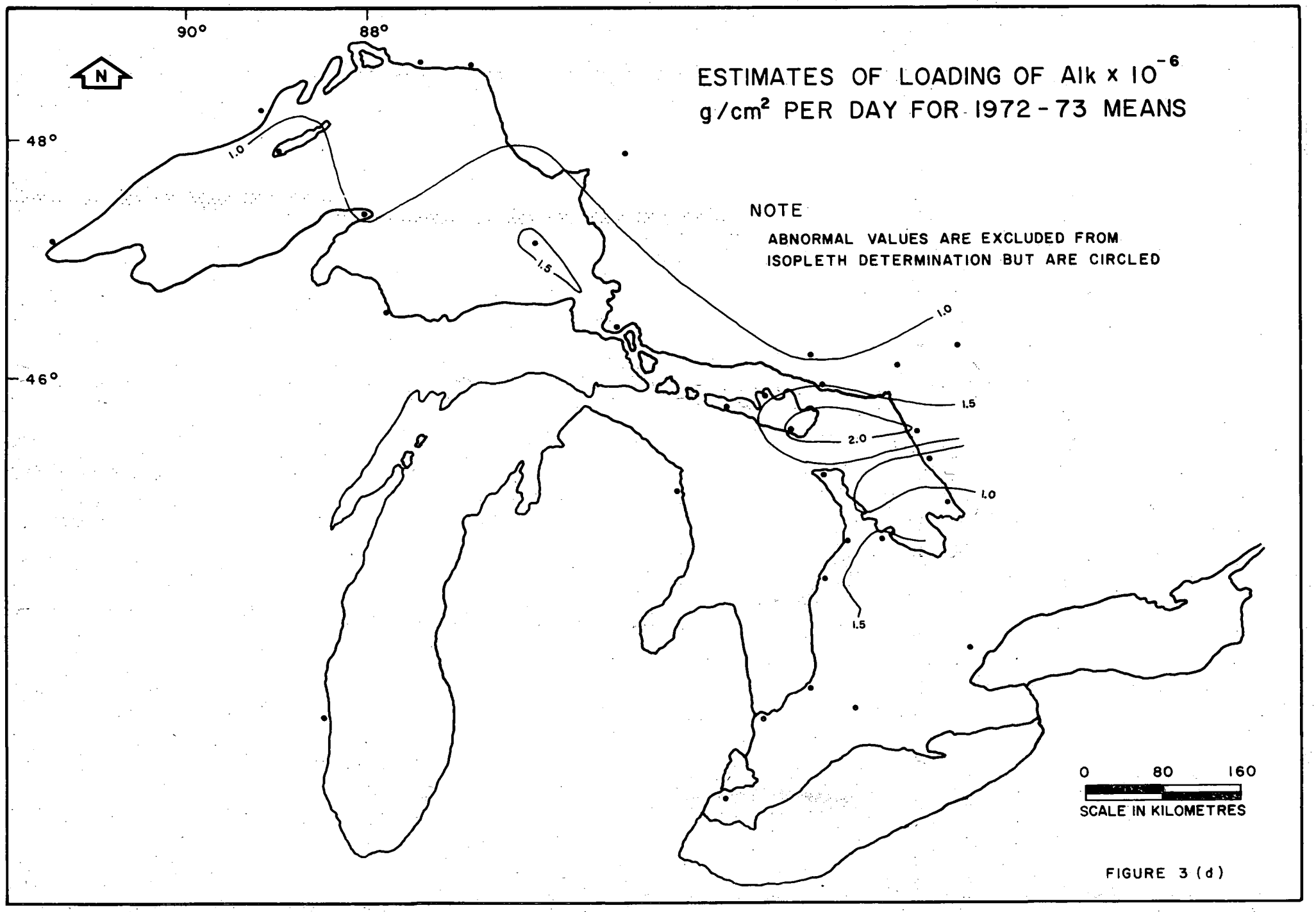

ESTIMATES OF LOADING OF Alk x 10^{-6}
g/cm² PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
90°
88°
48°
46°
N
1.0
1.5
2.0
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (d)

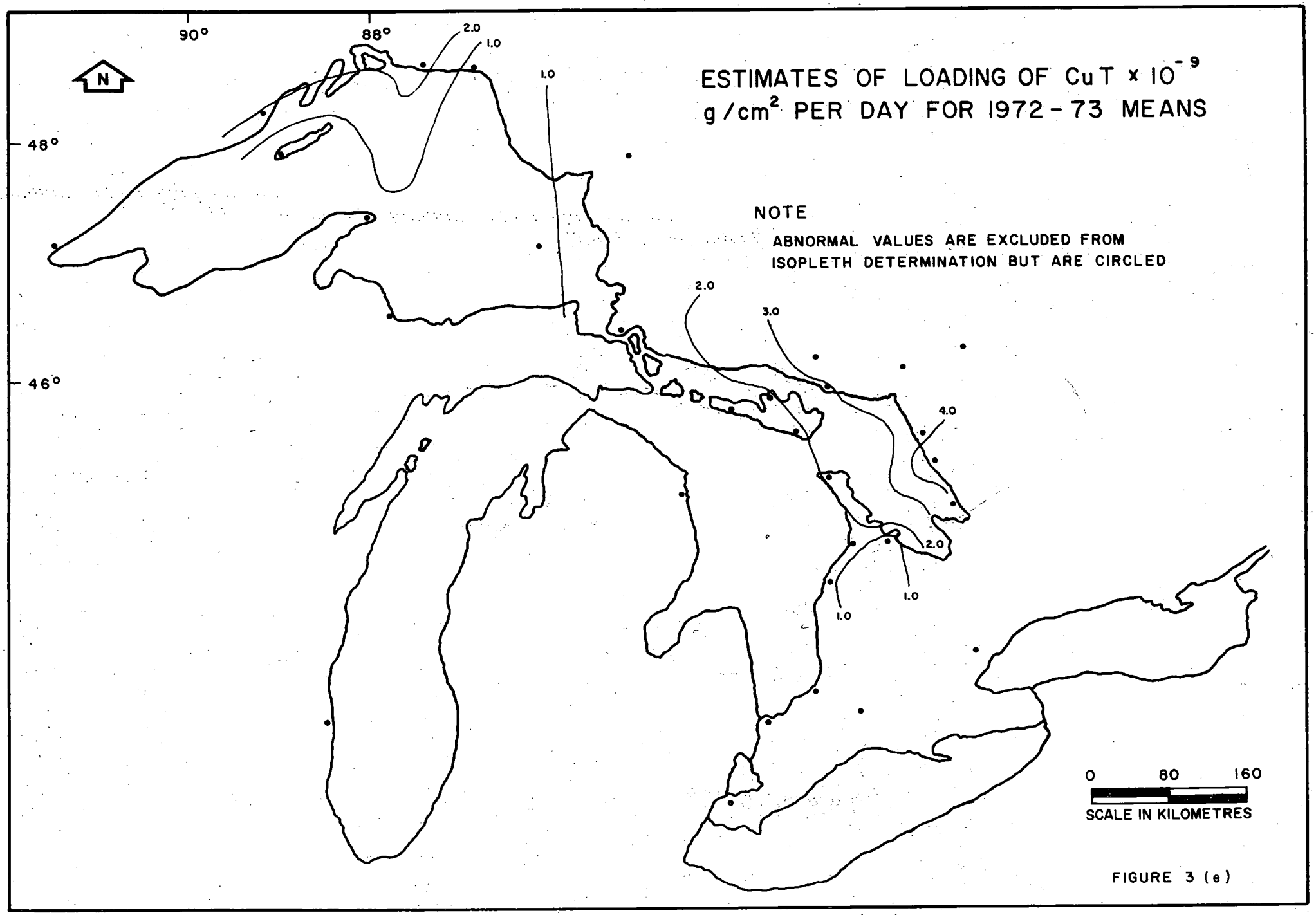

ESTIMATES OF LOADING OF CuT x 10^-9
g/cm² PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
2.0
1.0
1.0
2.0
3.0
4.0
2.0
1.0
1.0
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (e)

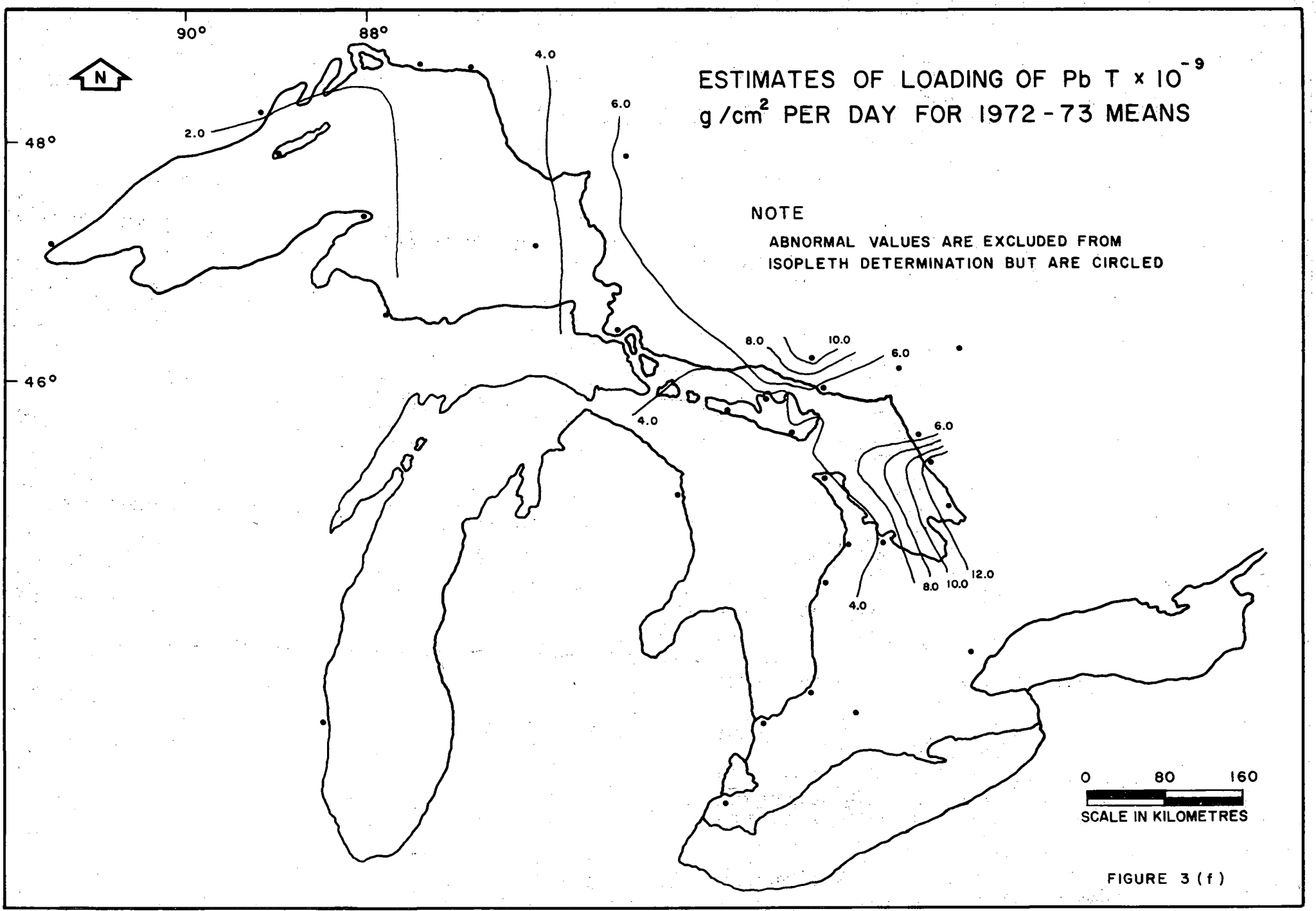

ESTIMATES OF LOADING OF Pb T x 10^-9
g/cm^2 PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
2.0
4.0
6.0
8.0
10.0
12.0
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (f)

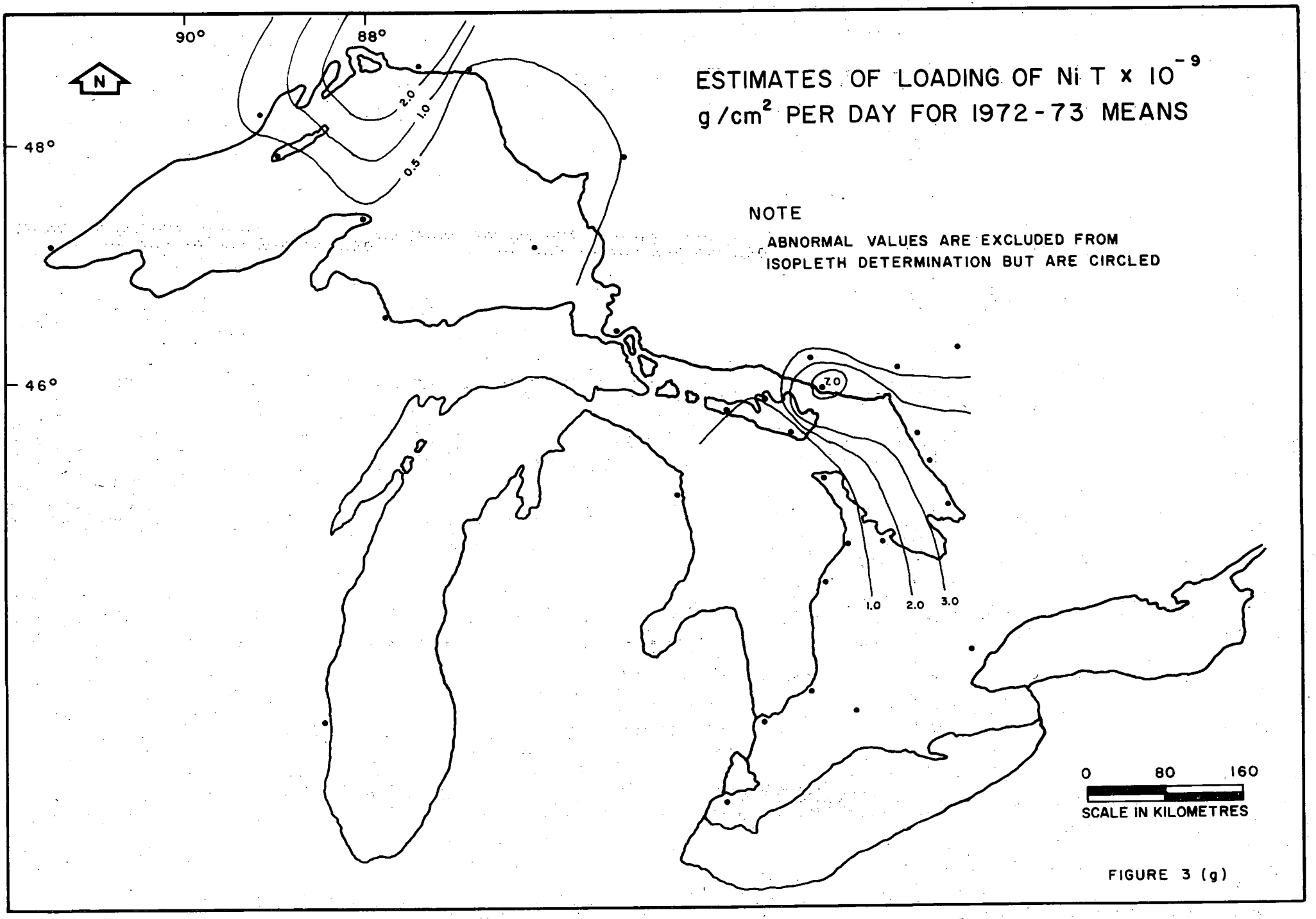

ESTIMATES OF LOADING OF Ni T x 10^{-9}
g/cm^2 PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
2.0
1.0
0.5
7.0
1.0
2.0
3.0
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (g)

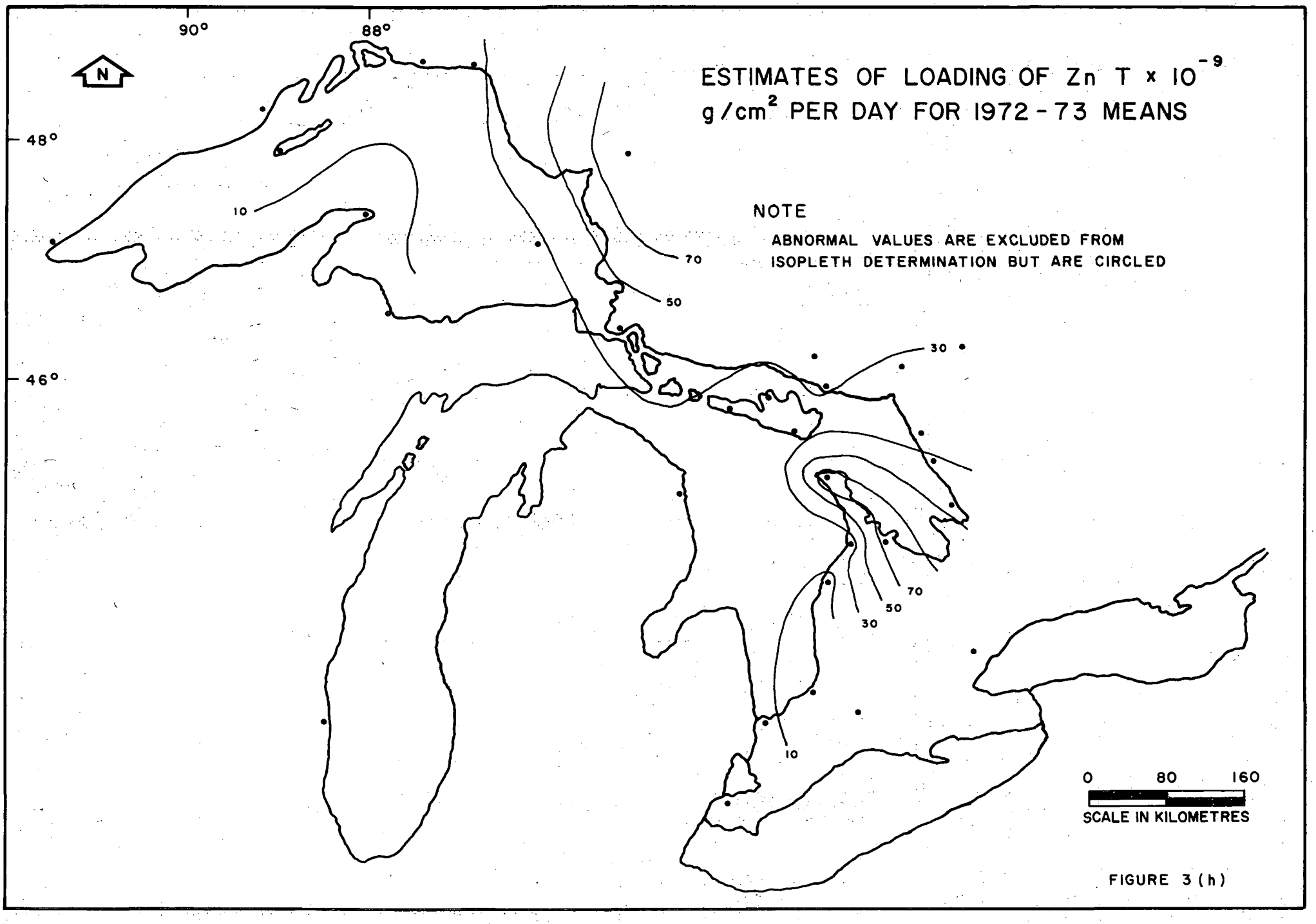

ESTIMATES OF LOADING OF Zn T x 10^{-9}
g/cm^2 PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM
ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
10
70
50
30
70
50
30
10
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (h)

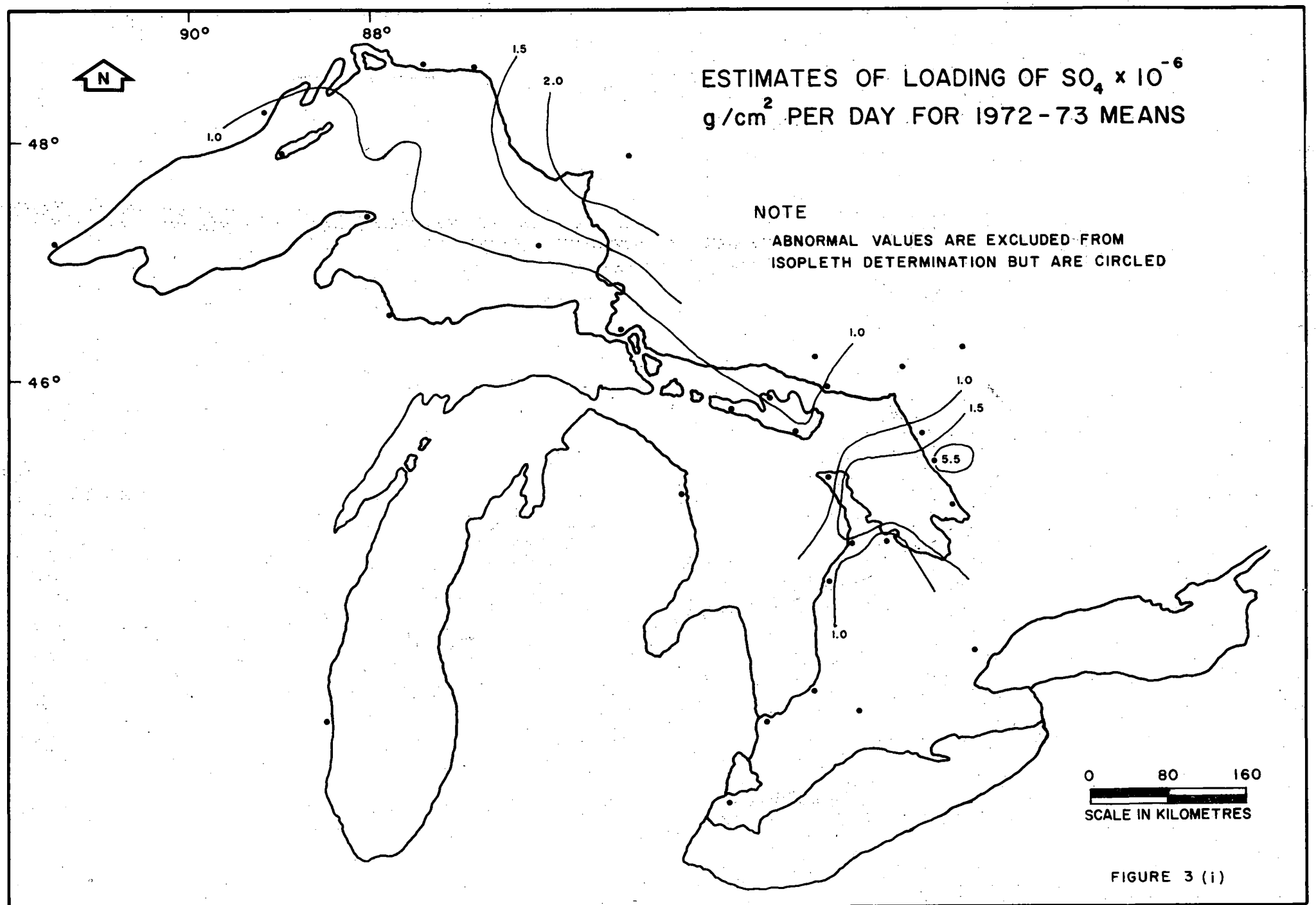

ESTIMATES OF LOADING OF $SO_4 \times 10^{-6}$ g/cm^2 PER DAY FOR 1972-73 MEANS
NOTE
ABNORMAL VALUES ARE EXCLUDED FROM ISOPLETH DETERMINATION BUT ARE CIRCLED
N
90°
88°
48°
46°
1.0
1.5
2.0
1.0
1.0
1.5
5.5
1.0
0
80
160
SCALE IN KILOMETRES

FIGURE 3 (i)

The average loading data for CCIW and McMaster, with the above exceptions, fit together to give a continuous pattern.

Interpretation:

Ignoring the listed exceptions, the following is a first (conservative) estimate of the average loading of commonly measured parameters for Lakes Superior and Huron.

	Superior	Huron
T PO_4	20	25×10^{-9} g/cm^2/day
NO_3	.15	$.3 \times 10^{-6}$
SiO_2	.2	$.4 \times 10^{-6}$
Alk	1.0	1.3×10^{-6}
Cu T	1.2	2.3×10^{-9}
Pb T	2.1	3.1×10^{-9}
Ni T	.5	$.8 \times 10^{-9}$
Zn T	17	20×10^{-9}
SO_4	1	1.3×10^{-6}

3.6 - Monthly Samples -
Yearly Estimates of Loading

From the previous table of estimates of loading, the following table of tentative estimates of yearly loading to Lakes Huron and Superior are calculated.

	Superior	Huron
	(Tons (2,000 lb)/year)	
T PO_4	7,000	5,000 (as CPO_4)
NO_3	50,000	70,000 (as CN)
SiO_2	70,000	100,000
Alk	330,000	310,000 (as $CaCO_3$)

	Superior	Huron
	(Tons(2,000 lb)/Year)	
Cu T	400	550
Pb T	700	740
Ni T	160	200
Zn T	6,000	5,000
SO_4	300,000	310,000

These estimates are considered to be conservative. Conversion factors to obtain yearly loading in tons per year for Lake Superior and Lake Huron are 331(a) and 239(a) where a is the loading rate in 10^{-9} g/cm^2/day.

3.7 - Monthly Data - Multivariate Analysis

Monthly loadings for a (particular) parameter are considered superpositions of loadings from individual sources. The rate of loading from a source depends upon the emission strength, distance from source to receptor, fraction of wind travel in source-receptor sector, number of precipitation events at receptor and number of precipitation events at source. A weighing factor is defined for each source, s_i, consisting of distance from source to receptor, d_i, fractional wind travel in sector (using wind velocities >3 mph), w_i, number of precipitation days at receptor (>0.1 in), n_i, and number of precipitation days at source, m_i:

$$S_i \left(\frac{w_i \; n_i}{d_i^2 \; m_i} \right)$$

A first approach considers four source regions: Chicago-Milwaukee, Detroit-Windsor-Cleveland, Toronto-Hamilton-Buffalo, and Sudbury-Timmins. w_i is obtained by the fractional average of wind speeds in the directional sector of source and receptor; a sector is defined as 45 degrees. d_i is an arbitrary map distance measure and n_i and m_i are cumulative days of rain during the measurement period where precipitation is equal or greater than 0.01-inch rain equivalent.

The precipitation stations weather data are obtained from the closest of the 11 meteorological stations and are:

Precipitation Station Number	3, 4, 5, 11, 13, 15, 20, 25, 35, 37, 110, 111, and 112.
Weather Station Number	07, 03, 07, 07, 02, 02, 04, 07, 03, 03, 04, 03, 01, and 01.
Precipitation Station Number	113, 120, 130, 131, 132, 133, 134, 135, and 137.
Weather Station Number	04, 04, 02, 51, 01, 01, 04, 04 and 07.

Weather data for sources for Chicago, Detroit, Buffalo, and Sudbury are 52, 06, 05 and 07.

Analysis is carried out for parameter P_j, for all sources and for all data by least squares:

$$P_j = S_1\left(\frac{w_1\ n_1}{d_1^2\ m_1}\right) + S_2\left(\frac{w_2\ n_2}{d_2^2\ m_2}\right) + S_3\left(\frac{w_3\ n_3}{d_3^2\ m_3}\right) + S_4\left(\frac{w_4\ n_4}{d_4^2\ m_4}\right)$$

Input to the regression analysis is P_j, w_i, n_i, m_i, and d_i. s_1--s_4 are determined, and the goodness of fit as represented by the multiple correlation coefficient indicates the adequacy of the model.

Additional runs considering only wind and wind and precipitation give an indication of the sensitivity of each variable in the analysis.

The actual analysis of 1972-73 data is in progress.

3.8 - Event/Ship Samples - Nature of Distributions

Figure 4 is a sketch map showing the ship track or location of 29 precipitation events that were sampled and analyzed by CCIW on board ship. The direction preceding the event number represents the average wind direction one day before and the day of sampling. Table 6 is an index to the sample data. Samples are arranged in chronologically increasing order.

Moments (2, 3, and 4) were determined as defined previously and cumulative plots were made on probability paper for log (10) transformed data. The moment data are shown in Table 7 and cumulative probability plots on Figure 5.

Interpretation

The data appear to be lognormally distributed.

3.9 - Event/Ship Samples - Washout Analysis

Based on the assumption that washout (plus rainout) can be represented as an exponential decay of the form:

$$C_t = C_o e^{-\lambda t}$$

Where:

C_t = concentration at time t;

C_o = concentration at time zero;

λ = washout coefficient;

t = time after start of rainfall.

The shipboard precipitation chemistry data were analyzed to determine washout coefficients. Figure 6 shows a typical sequence of sampling. Estimates of the coefficient are superimposed.

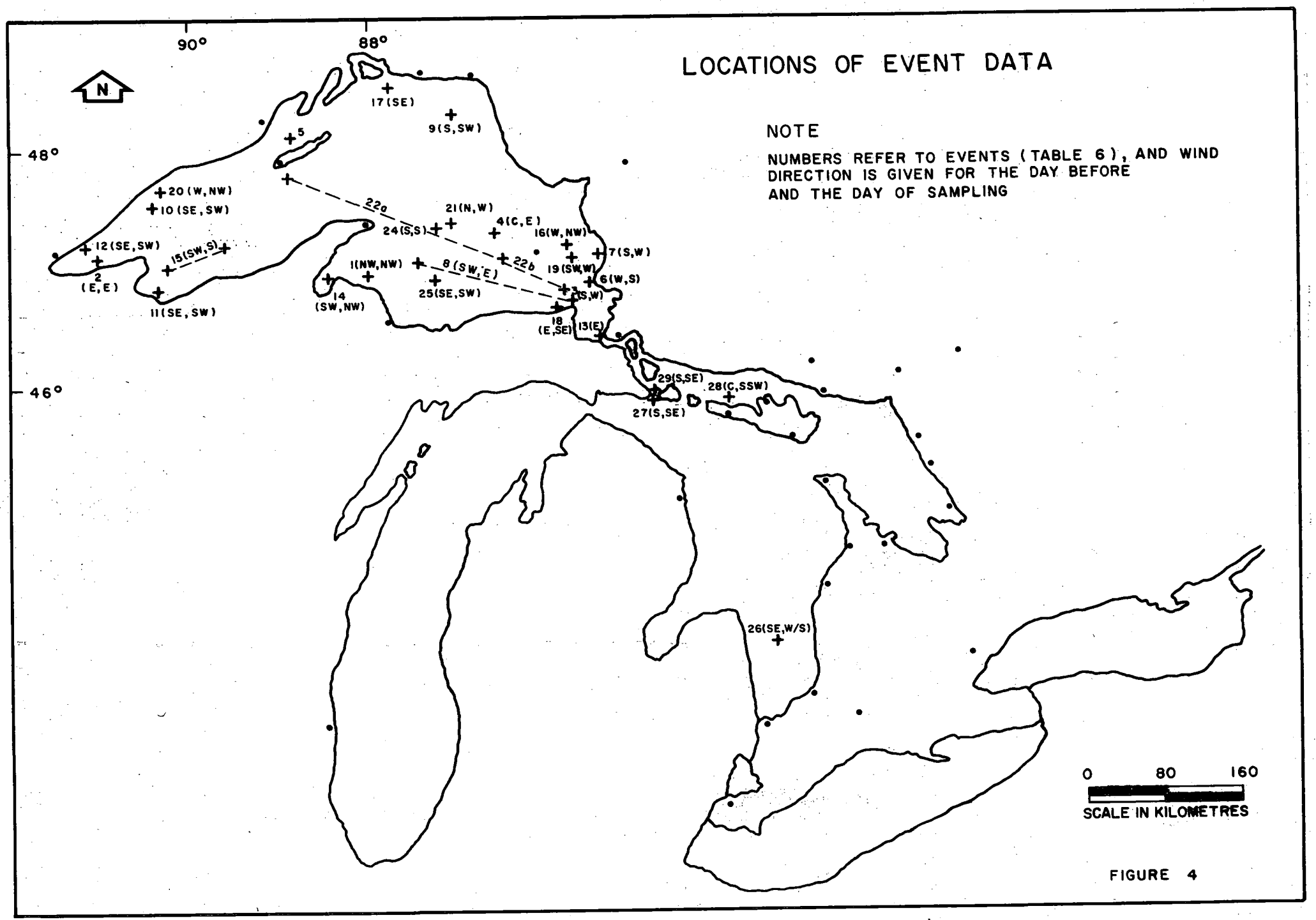

LOCATIONS OF EVENT DATA
NOTE
NUMBERS REFER TO EVENTS (TABLE 6), AND WIND DIRECTION IS GIVEN FOR THE DAY BEFORE AND THE DAY OF SAMPLING
N
90°
88°
48°
46°
17(SE)
9(S,SW)
5
20(W,NW)
10(SE,SW)
22a
21(N,W)
4(C,E)
24(S,S)
16(W,NW)
7(S,W)
12(SE,SW)
15(SW,S)
1(NW,NW)
8(SW,E)
22b
19(SW,W)
6(W,S)
2
(E,E)
25(SE,SW)
3(S,W)
14
(SW,NW)
11(SE,SW)
18
(E,SE)
13(E)
29(S,SE)
28(C,SSW)
27(S,SE)
26(SE,W/S)
0
80
160
SCALE IN KILOMETRES

FIGURE 4

TABLE 6

RELATIONSHIP OF EVENTS AND SHIP SAMPLES OF PRECIPITATION IN LAKES SUPERIOR AND HURON - (See Figure 4 for Locations) 1973

Event Number	Beginning Date	Time	Sample Number	
1	May 16	0430	1	Lake Superior
2	May 22	1600	2	Lake Superior
3	May 30	2300	3	Lake Superior
4	June 3	1800	4,5	Lake Superior
5	June 6	2340	6	Lake Superior
	June 7	1200	7	Lake Superior
	June 8	1200	8	Lake Superior
6	June 10	0500	9 - 11	Lake Superior
7	June 11	0130	12	Lake Superior
8	June 16	1300	13	Lake Superior
	June 17	1530	14	Lake Superior
	June 17	2300	15	Lake Superior
	June 19	0930	16	Lake Superior
	June 19	1400	17	Lake Superior
9	June 20	1000	18	Lake Superior
10	June 25	1300	19	Lake Superior
11	June 26	0300	20	Lake Superior
12	June 26	2200	21	Lake Superior
13	July 27	0030	22	Lake Superior
14	July 30	1300	23	Lake Superior

Event Number	Beginning Date	Time	Sample Number	
15	August 6	0700	24	Lake Superior
	August 6	1200	25	Lake Superior
	August 7	1500	26	Lake Superior
16	August 14	0030	27	Lake Superior
17	August 16	1230	28	Lake Superior
	August 16	2030	29	Lake Superior
18	August 19	1700	30	Lake Superior
19	August 23	0700	31	Lake Superior
20	September 15	1700	32	Lake Superior
21	September 17	1930	33	Lake Superior
22	October 3	2330	34	Lake Superior
	October 4	1930	35	Lake Superior
24	October 25	2330	36	Lake Superior
25	November 21	2100	38	Lake Superior
26	May 9	2230	39	Lake Huron
27	July 26	1400	40	Lake Huron
28	September 18	2000	41, 42	Lake Huron
29	October 13	0840	43	Lake Huron

TABLE 7

MOMENT ANALYSIS OF CONCENTRATIONS
OF SHIP SAMPLES FROM LAKE SUPERIOR
AND HURON, 1973
(Only Values Greater Than Zero Are Considered)

Variable	Size	Variance	Skewness	Kurtosis	Standard Deviation
PO_4 (P)	17	1070	1.2	6.9	33
log (10)	17	.18	-.5	2.2	.42
T N	33	1690000	1.4	1.4	1300
log (10)	33	.05	.06	.55	.23
Alk	23	2000000	.3	.14	1400
log (10)	23	.18	-.57	1.3	.42
PO_4 R(P)	42	8800	2.7	31	94
log (10)	42	.37	.1	-.15	.61
NO_3 R	43	91000	.92	3.6	302
log (10)	43	.11	-.05	-.25	.33
NH_3	43	52000000	3.1	38	7200
log (10	43	.23	.93	5.8	.48
Cl	39	7000000	1.5	11	2600
log (10)	39	.15	.27	.24	.39
SiO_2	42	6300	1.4	9.3	79
log (10)	42	.13	.13	.64	.36

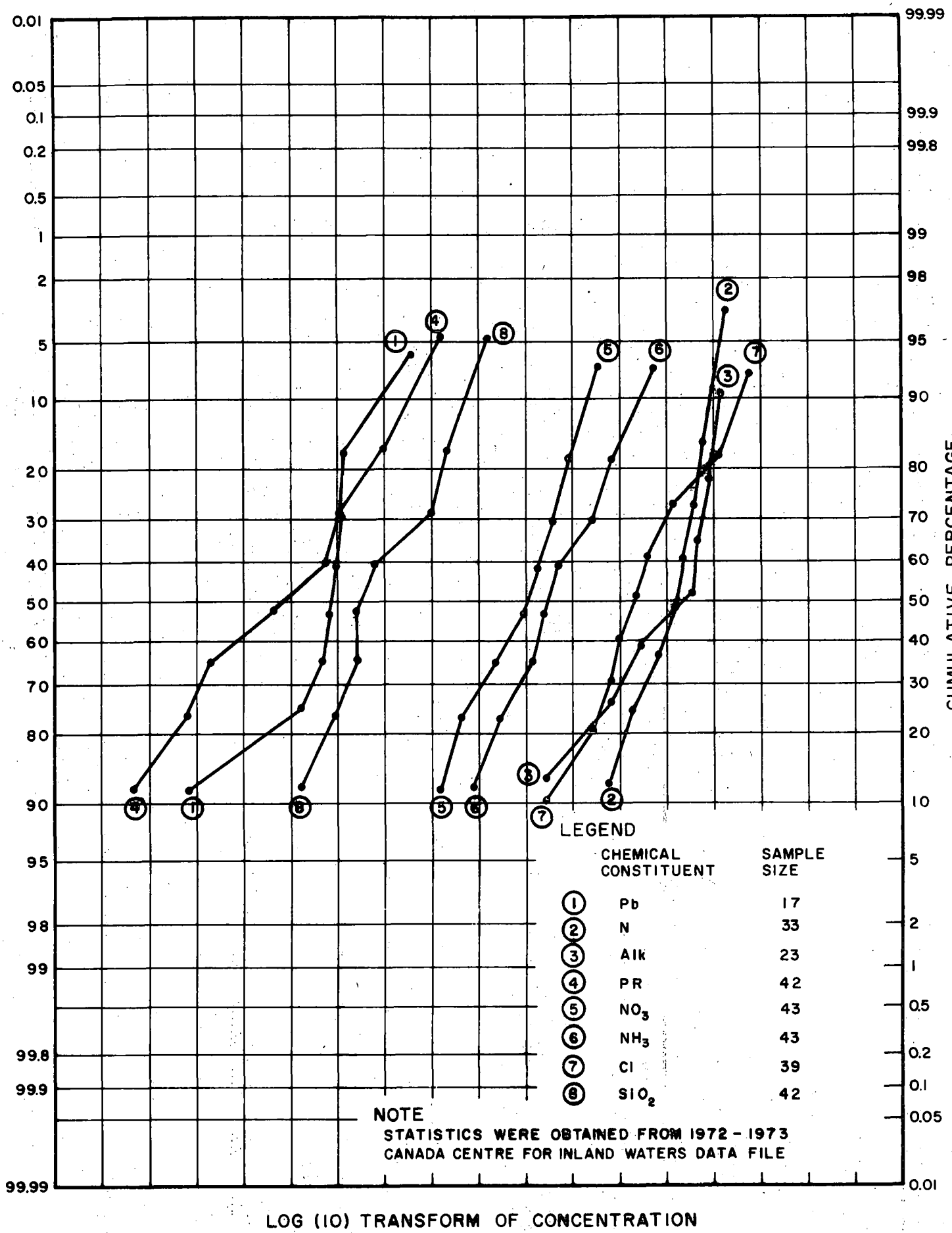


FIGURE 5

UPPER LAKES EVENT DATA, CONCENTRATIONS

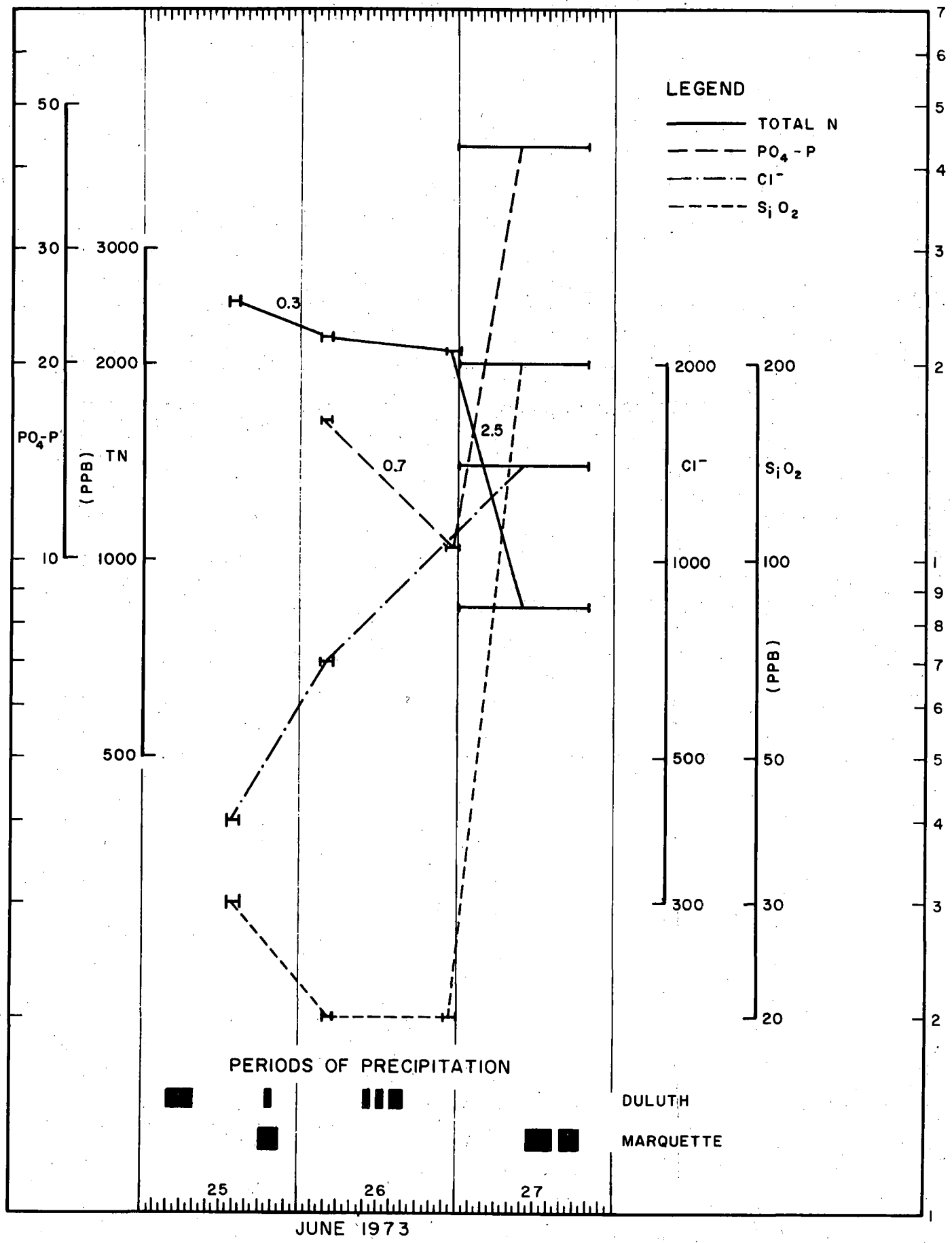


FIGURE 6

WASHOUT COEFFICIENTS FOR SHIP SAMPLES

In all, ten values were estimated for total-N and five for PO_4-P. These are as follows:

Total-N	PO_4-P
1.1×10^{-5} sec^{-1}	$.9 \times 10^{-5}$ sec^{-1}
0.2	.7
0.5	.7
0.8	.6
2.7	>2.7
0.2	
0.3	
0.3	
2.5	
1.7	
Median 0.65×10^{-5} sec^{-1}	0.7×10^{-5} sec^{-1}

Washout and rainout coefficients as determined by other workers are tabulated below:

	Washout (sec^{-1})	Rainout (sec^{-1})	Material
Engelmann (1965)	1.6×10^{-4} $J^{0.8}$	-	-
Makhon'ko (1967)	10^{-5}-10^{-4}	10^{-4}-10^{-3}	Aerosols
Perkins et al (1970)	-	10^{-4}-5×10^{-3}	Radio-nuclides
Beilke (1970)	10^{-4}-10^{-3}*	-	NO_2
Beilke (1970)	10^{-4}-10^{-2}*	-	SO_2
Hidy (1971)	10^{-8}-10^{-3}**	10^{-4}-10^{-2}**	Aerosols
Esmen (1972)	$.3$-$.8 \times 10^{-5}$	-	Particulates
Dana et al (1973)	$.7 \times 10^{-5}$ J	-	Sulphate

*Range is a function of rainfall intensity and droplet radius.
**Range is a function of particle size.
J = rainfall rate in mm/hr^{-1}.

For all events examined, except one, Cl^- concentrations were found to increase during the events. The reason for this is unknown. Data were also available for silica. These showed no outstanding characteristics.

3.9.1 - Bibliography for Section 3.9

Beilke, S. (1970). "Laboratory Investigations on Washout of Trace Bases", Precipitation Scavenging (1970),U.S. AEC.

Dana, M.T., J.M. Hales, W.G.N. Slinn and M.A. Wolf (1973). Natural Precipitation Washout of Sulfur Compounds from Plumes, EPA.

Engelmann, R.J. (1965). The Calculation of Precipitation Scavenging, USA EC Report, Battelle - Northwest Laboratory.

Esmen, H.A. (1972). "Particle Retention Efficiency of Scavenging Rainfall", Paper Presented to Div. Water, Air and Waste Chemistry, Am. Chem. Soc., Boston.

Hidy, G.M. (1971). "Theoretical Models for Aerosol Behavior", Particulate Models: Their Validity and Application, NCAR Boulder, Colorado.

Perkins, R.W., C.W. Thomas, J.A. Young and B.C. Scott (1970) "In-Cloud Scavenging Analysis from Cosmogenic Radionuclide Measurements", Precipitation Scavenging (1970), U.S. AEC.

Makhon'ko, K.P. (1967). "Simplified Theoretical Notion of Contaminant Removal by Precipitation from the Atmosphere" Tellus, Vol. 19, No. 3, pp. 467-476.

3.10 - Event/Ship Samples - Grouping by Location

Discriminant function analysis was carried out on ship samples. Events were grouped as follows:

(a) West Superior: 2, 19, 20, 21, 24, 25, 26, 31, and 32.

(b) North Superior: 6, 7, 8, 18, 23, and 29.

(c) Southeast-East Superior: 1, 3, 4, 5, 9, 10, 11, 12, 13, 14, 15, 16, 17, 22, 23, 27, 30, 33, 34, 36, 36, and 38.

(d) North Channel: 40, 41, 42, and 43.

Reactive phosphate, reactive nitrate, and ammonia were the variables considered. The discriminant function analysis suggested that there was no significant difference between groups by area. Rearrangement into Lake Superior and Lake Huron groupings suggested that there was even poorer discrimination.

Interpretation

There appears to be no difference in concentration, distributions from one portion of the Upper Lakes to another.

3.11 - Event/Ship Samples - Grouping by Source

The event concentrations were arranged as negligible source, possible source, and definite source by estimating average wind directions for the day preceding and the day of the sampling. For both lakes a northwest wind sector was considered negligible additions, a southeast sector and southwest sector was considered definite for Superior and Huron respectively, and a southwest sector and a southeast sector was considered possible for Superior and Huron respectively. Grouping of the events using these criteria resulted in:

Definite: Events 2, 4, 8, 11, 13, 17, 18, 23, 25, 26, 27, 28 and 29.

Possible: Events 3, 5, 6, 7, 9, 10, 12, 15.

None: Events 1, 14, 16, 20, 21 and 23.

Data for reactive phosphate, reactive nitrate, and ammonia were subjected to discriminant function analysis. The results suggested a definite separation of the "none" group, but the definite and possible source groupings were mixed.

Interpretation

Sources can be isolated on a statistical basis by separating north-northeast-northwest sources from all other sources.

3.12 - Event/Ship Samples - Comparison to Monthly Data

Two group discriminant function analyses was carried out for the variables total nitrogen, total phosphate, reactive phosphate, reactive nitrate, ammonia, chloride, and reactive silica to ascertain whether there is any difference between ship data and shore data. Only ship and shore data for Lake Superior were considered; shore data from Caribou Island was eliminated. This culling resulted in 28 sets of ship data and 52 sets of shore data.

Discriminant function analyses for the two groups and six variables shows that there is no significant difference between the two groups of data. The chi-square test suggests that the means for the six variables in the two groups are the same at the 99 per cent confidence level. Group classification by discriminant function resulted in 16/28 lake data classified in that group and 40/52 shore stations classified in the shore group.

Interpretation

There is no significant difference between monthly concentration data collected onshore and individual event samples collected on ship after inconsistently high data are first removed (e.g. Caribou Island).

4 - EMISSIONS DATA

4 - EMISSIONS DATA

The purpose of the emissions inventory is to assess the relative and absolute source strengths of various emission types. This information will be the basic input into the proposed predictive model. Tables 8 and 9 give 1973 emission estimates for particulates, oxides of sulphur and nitrogen, hydrocarbons and carbon monoxide.

Methodology is discussed in the following sections, both in relation to Tables 8 and 9 and for estimating source values for the heavy metals and other loadings. The latter estimates will be made early in Phase Two.

4.1 - Method of Analysis

Air emissions data for the five major pollutants from all significant stationary and non-stationary sources (particulates, oxides of sulphur, oxides of nitrogen, hydrocarbons and carbon monoxide) were documented for the Province of Ontario and States bordering the Great Lakes. In the case of the United States data, the emissions data were for 1973, and were provided by the United States Environmental Protection Agency and by Air Quality Control Region. Data on a county basis were also obtained from some of the State agencies.

The basis for the Canadian data is the 1970 information contained in a Nationwide Inventory of Air Pollutant Emissions, Acres (1972), for Environment Canada using 1970 as the base year. Data were then updated to expected 1973 levels in consultation with Air Management Branch, Ontario Ministry of the Environment.

Table 8 defines the principal areas of concern by type of emissions. There are eight primary areas (Figure 7) which are:

(1) Chicago-Gary-Milwaulkee

(2) Green Bay

(3) Detroit-Windsor-Cleveland-Toledo-Sarnia

(4) Toronto-Hamilton-Buffalo-Niagara-Rochester-Erie

TABLE 8

1973 EMISSIONS - PRIMARY SOURCES
(Thousand Tons per Year)

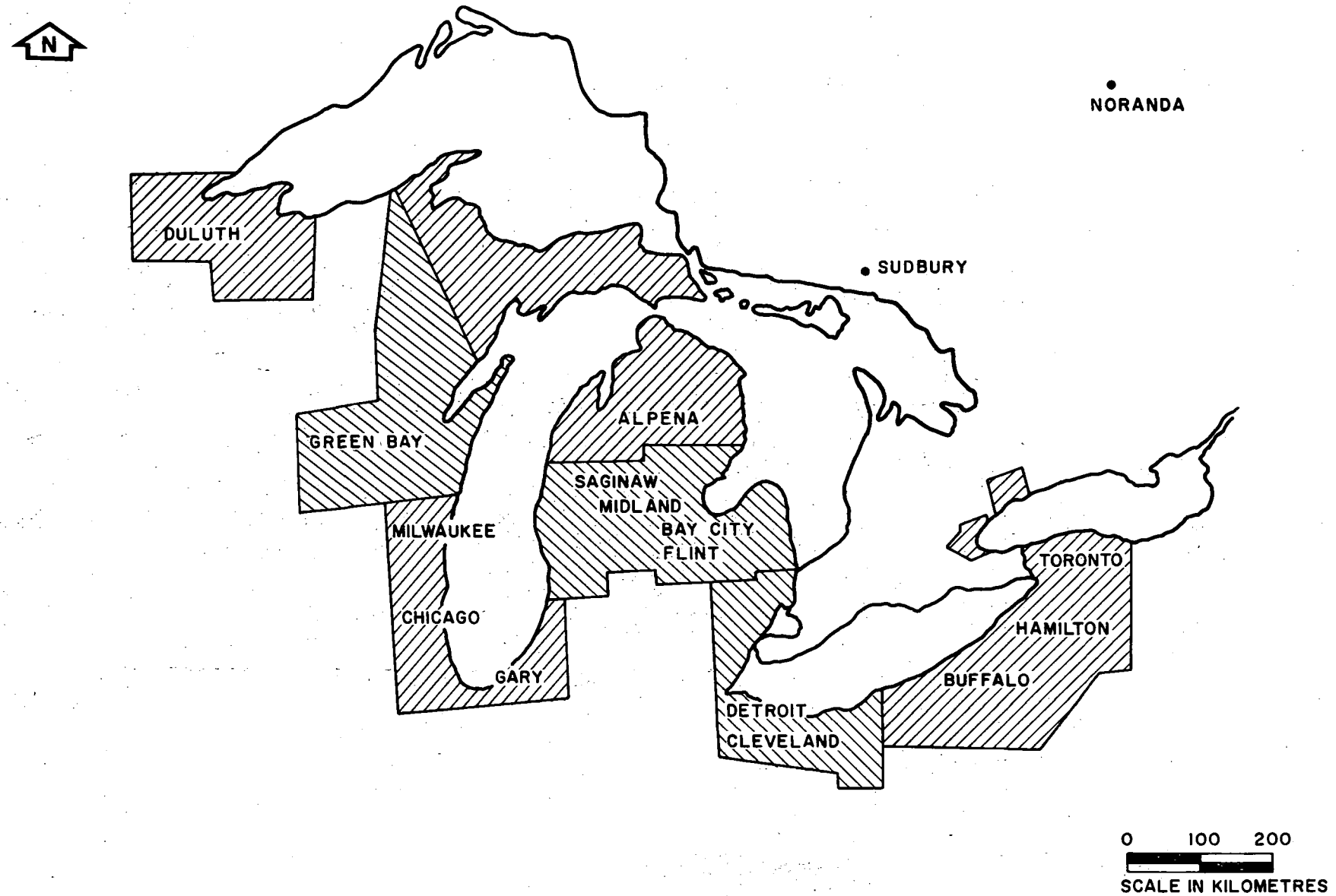
Complex	Particulates	SO_x	NO_x	Hydrocarbons	CO
1 - Chicago-Gary-Milwaukee	874	1,519	1,526	1,393	4,403
2 - Green Bay	117	195	114	78	363
3 - Detroit-Windsor-Cleveland-Toledo-Sarnia	997	1,882	2,489	984	4,390
4 - Toronto-Hamilton-Buffalo-Niagara-Rochester-Erie	586	1,233	575	325	2,348
5 - Sudbury-Noranda	32	2,670	-	-	-
6 - Saginaw-Midland-Bay City-Flint	196	573	245	201	983
7 - Duluth-Superior	109	137	63	47	45
8 - Alpena-Sault Ste. Marie	105	65	47	125	200
TOTAL	3,016	8,274	5,059	3,153	12,732

TABLE 9

1973 EMISSIONS - FRINGE AREAS*
(Thousand Tons per Year)

	Particulates	SO_x	NO_x	Hydrocarbons	CO
1 - Minnesota	156	265	250	358	1,411
2 - Wisconsin	239	323	236	230	1,038
3 - Illinois	1,088	3,167	1,213	1,451	5,875
4 - Indiana	711	1,568	540	545	2,196
5 - Michigan	52	103	101	126	521
6 - Ohio	1,406	2,606	895	725	3,304
7 - Pennsylvania	1,947	3,263	3,405	1,247	4,637
8 - New York	161	325	349	337	1,603
9 - Ontario	126	296	114	426	1,782
TOTAL	5,886	11,916	7,103	5,445	22,367

*Remaining emissions by State and Ontario outside the primary source areas.



PRIMARY SOURCE AREA EMISSIONS FIGURE 7

(5) Sudbury-Noranda

(6) Saginaw-Midland-Bay City-Flint

(7) Duluth-Superior

(8) Alpena-Sault Ste. Marie.

The remainder of the States and the Province of Ontario are included in the table on Emissions for Fringe Areas (Table 9).

4.1.1 - Ontario Emissions Data

The data included for areas in Ontario were estimated for the five pollutants on the basis of an anticipated overall decrease in these emissions. This trend toward overall decrease will be confirmed with the release of the actual 1973 emissions which will be available early in Phase Two. The 1973 emissions data are now being processed.

4.2 - A Method for Estimating Other Loadings

At the present time, few published emissions for heavy metals are available. It will be assumed, for the purpose of analyzing the presence of heavy metals, that they are included in the readings for particulates, but in an undifferentiated form.

Industrial processes will be identified relative to their potential for emitting the heavy metals in question. It will be necessary to derive information on industrial and other processes in terms of their total production of finished products and their total input of fuel, for example.

The requirements for this study are in terms of determining the amounts of iron, lead, copper, cadmium, nickel* in the total of particulate emissions by most probable process sources.

The study conducted by Vandegrift et al (1971)** identified, characterized, and quantified particulates by stationary sources. In short, the total tonnage emitted by a given industry was based on the total tonnage processed per year by the industry, the efficiency of control equipment used, and the percentage of production capacity equipped with control devices.

The methodology developed by Vandegrift will be useful in the identification of particulate types emitted, relative to the type or types of processes most likely to emit them. The aforementioned study operated on the basis of national data. Data on a regional or subregional basis will require additional detailed analysis,and this work is being carried out.

The probable sources of information on industrial production for the United States will be the Census of Manufacture and the Census of Transportation by Commodity by selected areas. In some cases where production data are not directly available, it will be necessary to utilize financial data on the various companies by type of industrial process and area to derive estimates of their production capacity. The Census information is available for 1967 and perhaps 1970, and will have to be updated to 1973.

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*Data are compiled for 4 of these metals by the Environmental Protection Service, Environment Canada, by provinces, but are not yet published. The compilations are available for data extraction. A similar requirement applies for estimating emissions of phosphorous, nitrate,ammonia, chloride, sulphate, calcium, magnesium, sodium and potassium.

**Vandegrift, A.E., L.J. Shannon, E.E. Sallee, P.G. Groman, and W.R. Park. "Particulate Air Pollution in the United States", Jour. APCA, Vol. 21, No. 6, p. 321. 1971.

There will be a need to identify processes other than industrial, e.g. agriculture, residential and commercial, etc., as sources for the areas under study.

Data sources in Canada are principally the SIC publications of Statistics Canada and the Operators Lists of Department of Energy, Mines and Resources, Canada.

5 - MATHEMATICAL MODELLING OF ATMOSPHERIC LOADINGS

5 - MATHEMATICAL MODELLING OF ATMOSPHERIC LOADINGS

5.1 - Introduction

In considering a predictive model to estimate atmospheric loading on the Upper Great Lakes, two aspects are of fundamental importance. The first relates to the transport and diffusion processes of a contaminant emitted into the atmosphere. The second concerns the depositional processes (wet, dry or gaseous) either en route or at the receptor (lakes).

Literature relating to these aspects has been reviewed. However, time precluded an in-depth study of the depositional processes. This will be completed early in Phase Two.

5.2 - Review of Transport Processes

In his text, Pasquill (1962) details the early work of Bosanquet and Pearson (1936), and Sutton (1947a,b). However, it was not until the early sixties that intensive research was initiated into the use of mathematical models for predicting pollutant levels in the atmosphere. For ease of review, the literature has been classified under seven headings. These are shown in Figure 8. Four are grouped under source-orientated models in which the contaminant concentration is calculated using the source strength and an appropriate mathematical algorithm. Under this group, we have included separately the 'box-type' models, steady-state point, line and area source Gaussian plume models, puff kernel Gaussian models, and those directly related to the fundamental transport diffusion equation. On the other hand, models under the receptor-orientated heading include those in which there are one or more 'free' parameters whose values are determined by minimizing a function relating observed to predicted concentrations. Three types have been differentiated. In Table 10, the models are classified under the seven headings. Model characteristics are presented in Tables 11 to 16.

In addition to the papers noted above, a number of review articles were cited - Gifford (1960), Moroz (1968), Stern (1970), Moses (1969), Calder (1969), Papetti and Gilmore (1971) and Munn (1971), as well as the proceedings of several

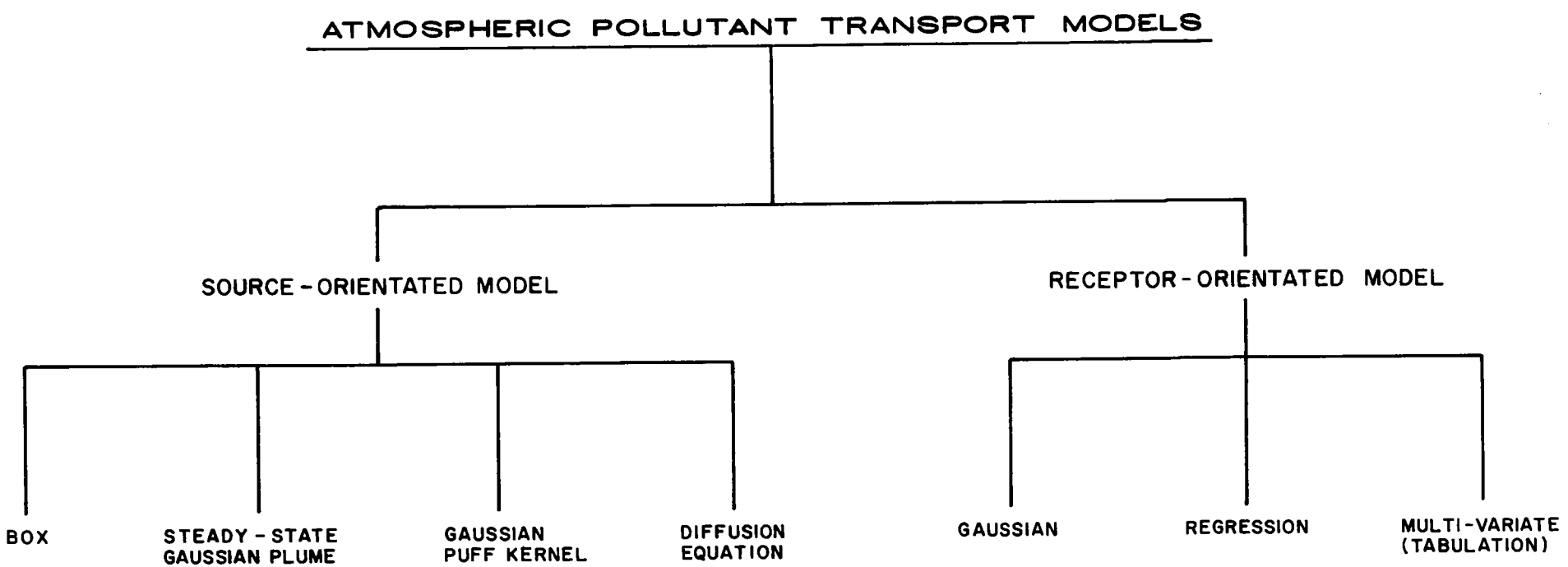
ATMOSPHERIC POLLUTANT TRANSPORT MODELS
SOURCE-ORIENTATED MODEL
RECEPTOR-ORIENTATED MODEL
BOX
STEADY-STATE GAUSSIAN PLUME
GAUSSIAN PUFF KERNEL
DIFFUSION EQUATION
GAUSSIAN
REGRESSION
MULTI-VARIATE (TABULATION)

FIGURE 8

TABLE 10

SUMMARY OF ATMOSPHERIC POLLUTANT TRANSPORT MODELS

Reference		Area	Pollutant
Bosanquet and Pearson	(1936)		
Sutton	(1947)		
Calder	(1949)		
Cramer	(1957)		
Frenkiel	(1958)	Los Angeles	
Monin	(1959)		
Pasquill	(1962)		
(1) Box Type			
Circular			
Slade	(1967)	Washington, DC/ Boston Axis	CO_2
Rodhe	(1972)	Europe	S
Rectangular			
Johnson et al	(1970)	Washington, DC	CO
Reiquam	(1970)	Europe	SO_2
Reiquam	(1971)	Oslo, Norway	SO_2
Ragland	(1973)		
(2) Steady-State Gaussian Plume			
Lucas	(1958)	London	SO_2
Pooler	(1961)	Nashville	SO_2
Turner	(1964)	Nashville	SO_2

Table 10 (Cont'd)

Reference		Area	Pollutant
Hilst and Bowne	(1966)	Fort Wayne, Indiana	Released Aerosol
Koogler et al	(1967)	Jacksonville, Florida	SO_2
Slade	(1967)	Washington, DC/ Boston Axis	CO_2
Hilst	(1968, 1969)	Connecticut	SO_2 and Others
Bowne	(1968)	Connecticut	SO_2
Johnson et al	(1970)	Washington	CO
Fortak	(1970)	Fortak, Germany	SO_2
Milford et al	(1971 a, b)	New York	SO_2
Shenfeld et al	(1972)	Toronto	SO_2, CO
Trent	(1973)	St. Louis	SO_2
(3) Gaussian Puff Kernel			
Davidson	(1967)	New York	SO_2
Shieh et al	(1970)	New York	SO_2
Roberts et al	(1970, 1971)	Chicago	SO_2
(4) Diffusion Equation			
Randerson	(1970)	Nashville	SO_2
Gifford and Hanna	(1971)	Bremen	SO_2
		Los Angeles	Natural Gas

Table 10 (Cont'd)

Reference		Area	Pollutant
Hanna	(1971)	Los Angeles Chicago	Natural Gas SO_2
Lamb and Neiburger	(1971)	Los Angeles	CO
Egan and Mahoney	(1972)		
Horie and Fan	(1973)	Chicago	
(5) Receptor-orientated Gaussian			
Clarke	(1964)	Cincinnatti	SO_2, NO_x
Pooler	(1966)	St. Louis	Tracer
Miller and Holzworth	(1967)	Nashville Washington Los Angeles	SO_2 NO_x NO_x
(6) Regression			
Miller	(1967)	Los Angeles Washington	NO_x
Roberts et al	(1968)	Chicago	
(7) Multivariate (Tabulation)			
Moses	(1969)		

TABLE 11

CHARACTERISTICS OF ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES: BOX MODELS

SLADE (1967)

$$\bar{\chi} = \frac{WQ}{H\left(\frac{2\pi r}{16} + y_1\right)\bar{u}} \cdot \exp\left(-\frac{0.693t}{T_{\frac{1}{2}}}\right)$$

Where:

W = fractional frequency of the wind direction into 16 direction sectors.

y_1 = diameter of circle of area equal to a particular county's area.

Area: 30 per cent larger than 160 km x 40 km.

REIQUAM (1970a)

$$C_{n,t} = (1/V_{n,t})[r_{n,t}\, q_{n,t} + R_{n,t}\, Q_{n,t}] + p_{n,t}\, C_{n,t-1}$$

Where:

$C_{n,t}$ = concentration

$V_{n,t}$ = volume of box

$q_{n,t}$ = rate of which pollutants are adverted into box n

$Q_{n,t}$ = emission rate within box n,

$r_{n,t}$ = residual of $q_{n,t}$ remaining

$R_{n,t}$ = residual of $Q_{n,t}$ remaining

$p_{n,t}$ = residual of $C_{n,t-1}$, remaining

$C_{n,t-1}$ = concentration in box n at time t-1

REIQUAM (1970a) (Cont'd)

Δt: 2 hr

Area: 16 x 16 grid (600m x 800m)

REIQUAM (1970b)

Algorithm as for previous reference.

Δt: 5 days

Area: Europe; sector 2°lat x 2° long

JOHNSON (1970)

$$\chi = \frac{Q(r_2-r_1)W}{\bar{u}H}$$

Δt: 24 hrs

Area: 32 - 1,000 km upwind of receptor

RODHE (1972)

$$D_i(r) = f_i\ Q\ (1-e^{-r/r_{oi}})$$

Where:

$D_i(r)$ = total deposition within distance r from source for sector i (45°)

f_i = frequency of occurrence of trajectory end points in each sector

r_{oi} = $V_i\ T_i$

V_i = average transport velocity from the source

T_i = turnover time

Area: Northern Europe

TABLE 12

CHARACTERISTICS OF ATMOSPHERIC
POLLUTANT TRANSPORT PROCESSES
STEADY-STATE GAUSSIAN PLUME MODELS

LUCAS (1958)

$$X_x = \frac{14\,Q}{\bar{u}} \left[\ln k + \frac{1}{k} - \frac{1}{k^2 . 2 . 2!} + \frac{1}{k^3 . 3 . 3!} \cdots \right]$$

Where:

$$k = \frac{0.00165\,x^2}{h^2}$$

h = effective chimney height

POOLER (1961)

$$\frac{X}{Q} = \frac{1.44 \times 10^{-5} \exp\left[-\frac{0.058\,u^{0.9}}{x^{1.5}} \right]}{u^{0.55}\,x^{1.75}}$$

$$\left(\frac{\overline{X}}{Q}\right)_{x,\theta} = \sum_{\bar{u}} f_{u,\theta} \left(\frac{X}{Q}\right)$$

Where:

$f_{u,\theta}$ = fractional wind frequency

Δt : monthly summary of hourly wind

Area : 80 square miles

TURNER (1964)

$$\frac{X}{Q} = \frac{\exp\left(-\frac{0.693\,t}{T^{1/2}}\right) \exp - \frac{1}{2}\left[\frac{y^2}{(\sigma_y + 402)^2} - \frac{(z-h)^2}{\sigma_z^2}\right]}{\pi \bar{u} (\sigma_y + 402)\,\sigma_z}$$

ΔT : 2 hours

Area: 9 miles x 11 miles; 1 mile intervals

HILST AND BROWN (1966)

$$D(x-x_0, 0) = \frac{Q}{\sqrt{2\pi}\,\bar{u}\left[\sigma_{z_0} + a(x-x_0)\right]} \exp\left\{-\frac{1}{2}\frac{z_0^2\, e^{-2\lambda(x-x_0)}}{\left[\sigma_{z_0} + a(x-x_0)\right]^2}\right\}$$

Where:

$D(x-x_0, 0)$ = dosage at a distance from line source of $x - x_0$

σ_{z_0} = standard duration of concentration at release level

a, λ = constants

KOOGLER ET AL (1967)

$$X = \frac{Q \exp\left(\frac{-0.693t}{T_{1/2}}\right) \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2 - \frac{1}{2}\left(\frac{z}{\sigma_z}\right)^2\right]}{\pi\,\bar{u}\,\sigma_y\,\sigma_z}$$

Area: 15 miles x 15 miles; 1 mile intervals

SLADE (1967)

$$X = \frac{Q}{(2\pi)^{1/2}\left(\sigma_{y_0}^2 + \sigma_y^2\right)^{1/2} H\,\bar{u}} \exp\left[-\frac{y^2}{2\left(\sigma_{y_0}^2 + \sigma_y^2\right)} - \frac{0.693t}{T_{1/2}}\right]$$

Where:

σ_y = 1/4 diameter of circle of area equal to a particular county's area

Area: 150 km x 40 km; grid 15 km apart

HILST (1968), BOWNE (1968)

(Travelers Research Center Model)

$$X = \frac{Q}{2\pi \bar{u}\, \sigma_y\, \sigma_z} \exp\left(-\frac{1}{2\,\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)$$

Area: State of Connecticut

JOHNSON (1970)

$$\frac{X}{Q} = \frac{0.8}{\bar{u}\, a}\,(1-b)^{-1}\left(r_{i+1}^{1-b} - r_i^{1-b}\right), \qquad b \neq 1$$

$$= \frac{0.8}{\bar{u}\, a}\,\ln\left(\frac{r_{i+1}}{r_i}\right), \qquad b = 1$$

Where:

a, b = constants related to stability

i = segment number

FORTAK (1970)

$$X = \frac{1}{2H}\sum_{n=1}^{N} \frac{Q_n}{\bar{u}_n} \exp\left(-\frac{t_n}{T_{1/2}}\right) \frac{\exp\left(\frac{\bar{y}_n^2}{2\,\sigma_{y,n}^2}\right)}{\sqrt{2\pi}\;\sigma_{y,n}}$$

$$\left[\theta\left(\frac{h_n - z}{2H}\,;\,\frac{\sigma_z^2}{2H^2}\right) + \theta\left(\frac{h_n + z}{2H}\,;\,\frac{\sigma_z^2}{2H^2}\right)\right]$$

Where:

θ = Jacobian theta function

Δt: 1/2 hour

Area: 625 sq km; 500 m x 500 m grid

TABLE 13

CHARACTERISTICS OF ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES: GAUSSIAN PUFF KERNEL MODELS

SHIEH ET AL (1970)

(New York University Model)

For an instantaneous point source:

$$X(x,y,z,t) = \frac{Q(t)}{(2\pi)^{3/2}\,\sigma_x(t)\,\sigma_y(t)\,\sigma_z(t)} \cdot$$

$$\exp\left\{-\frac{1}{2}\left[\left(\frac{x-ut-x'}{\sigma_x(t)}\right)^2 + \left(\frac{y-vt-y'}{\sigma_y(t)}\right)^2 + \left(\frac{z-wt-z'}{\sigma_z(t)}\right)^2\right]\right\}$$

Where:

u, v, w = velocities in x, y and z directions

x', y', z' = portion of release

Algorithms for continuous point and area sources are given in the paper:

Δt: 2 hours

Area: 30 miles x 40 miles; grid interval 0.5 - 5 miles

ROBERTS ET AL (1971)

(Argonne Research Laboratory Model)

$$G(x,y,z,t-t') = \exp - \left\{\frac{[x-u(t-t')]^2}{2(\sigma_x^2)^2} + \frac{y^2}{2(\sigma_y^2)^2} + \frac{z^2}{2(\sigma_z^2)^2}\right\} \left[(2\pi)^{3/2}\sigma_x\,\sigma_y\,\sigma_z\right]^{-1}$$

$$X(x,y,z,t) = \int_0^t dt'\, Q(t')\, G(x,y,z,t-t')\, \exp\left(-0.693\,\frac{t-t'}{T_{1/2}}\right)$$

Where:

t' = time of release of puff

Δt: 1 hour.

TABLE 14

CHARACTERISTICS OF ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES: DIFFUSION EQUATION

RANDERSON (1970)

$$\Delta C_d^n = K_A \left[C(i+1, j, k) - 2C(i,j,k) + C(i-1, j, k)\right]$$

$$+ K_B \left[C(i,j+1,k) - 2C(i,j,k) + C(i,j-1,k)\right]$$

$$- \frac{\Delta t}{2\Delta z^2} \left[K(i,j,k+\tfrac{1}{2})\right]\left[C(i,j,k+1) - C(i,j,k)\right]$$

$$- \frac{\Delta t}{2\Delta z^2} \left[K(i,j,k-\tfrac{1}{2})\right]\left[C(i,j,k) - C(i,j,k-1)\right]$$

Where:

ΔC_d^n = change in C due to the process of diffusion for time $t+\Delta t = n$

$K_A = \frac{\Delta t}{2\Delta x^2} K(x)$

$K_B = \frac{\Delta t}{2\Delta y^2} K(y)$

K = exchange coefficient of pollutant

Area: 12 miles x 11 miles; 1-mile intervals

GIFFORD AND HANNA (1971)

$$X_0 = \frac{z_1^m \left(\frac{1}{2}\Delta x\right)^{1-s}}{c_1 u B(1-s)} \left\{ Q_0 + \sum_{i=1}^{N} Q_i \left[(2i+1)^{1-s} - (2i-1)^{1-s} \right] \right\}$$

Where:

$$s = \frac{m+1}{2+m-n}$$

$$x = \left(N + \frac{1}{2}\right) \Delta x$$

N = number of upwind grid squares in source inventory

Δx = grid size

$$u(z) = u_1 \left(\frac{z}{z_1}\right)^m$$

$$K(z) = K_1 \left(\frac{z}{z_1}\right)^n$$

c_1 is related to stability

B = constant

K = eddy diffusivity

HANNA (1971)

$$X = C \frac{Q_0}{\bar{u}}$$

Where:

$$C = \sqrt{\frac{2}{\pi}} \left(\frac{2N+1}{2} \Delta x \right)^{1-b} \frac{1}{a(1-b)}$$

a, b are related to stability

LAMB AND NEIBURGER (1971)

The working equations are based on the following diffusion equation:

$$\frac{\partial C}{\partial t} + U(x,y,t)\frac{\partial C}{\partial x} + V(x,y,t)\frac{\partial C}{\partial y} = LC + f(t)C + S(x,y,z,t)$$

with boundary conditions:

$$C(x,y,z,o) = I(x,y,z)$$

$$\lim_{x,y \to \pm\infty} C(x,y,z,t) = 0$$

$$\frac{\partial}{\partial z} C(x,y,o,t) = o; \quad \frac{\partial C}{\partial z} = -\beta C, \quad z = h$$

Where:

I = initial concentration

U,V = x and y components of surface wind

β = constant

f(t) = allows for chemical reaction in which reaction speed is proportional to concentration

S = distribution of pollutant

L = differential operator which describes the time rate of change of mean concentration due to turbulence

Δt: 200 secs

Area: About 25,000 sq km

HORIE AND FAN (1973)

$$\frac{dX}{dt} = -RX + Q$$

Where:

X = total amounts of pollutants in the atmosphere per unit ground level

$= \int_0^H C dz = BH\, C_g$

R = dilution factor

$= -\frac{1}{B} \left\{ \frac{K_z(H)}{H^2} \cdot \frac{df}{d\xi}\Big|_{\xi=1} - \frac{m(\theta)E}{L} U(H) + f(1) \frac{d \ln H}{dt} \right\}$

Q $= \int_0^H (q + \phi)\, dz$

B $= \int_0^1 f(\xi)\, d\xi$ varies between 1/2 and 1

E $= \int_0^1 \xi^p f(\xi)\, d\xi$ varies between 0.27 and 0.83

ξ = z/H

$m(\theta)$ = wind direction factor of the urban area

$= \{7 - (C_{gf} U_{rf} / C_g U_r)\} / d(\theta)$

$d(\theta)$ = geometrical direction factor of the urban area

$= S_g / WL$

θ = main wind direction

W = width of the urban area which is normal to the main wind direction

L = characteristic size of the urban area

C = mass concentration of pollutant

K_z = eddy diffusivity in z direction

q = rate of emission per unit volume

ϕ = rate of dissipation or production due to precipitation or photochemical reaction per unit volume

H = mixing depth

$U(z) = U_r \left(\frac{z}{z_r}\right)^p$, $0.2 \geqslant p \geqslant 0.5$

$C(z) = C_g\ f\ (z/H)$

U_r = wind velocity at reference height z_r

p = exponent dependent on stability

C_g = ground level concentration

f = arbitrary profile function of concentration

TABLE 15

CHARACTERISTICS OF ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES: RECEPTOR ORIENTATED GAUSSIAN MODELS

CLARKE (1964)

$$\frac{X}{Q} = \frac{2}{\sqrt{2\pi}\,\bar{u}(\pi/8)\,x\,\sigma_z} \exp\left(-\frac{1}{2}\frac{z^2}{\sigma_z^2}\right) \exp\left(\frac{0.693t}{T_{1/2}}\right)$$

Area: 22-1/2° sectors at radii of 1, 4 and 16 km

POOLER (1966)

$$\frac{X}{Q} = \frac{1}{\pi\bar{u}(\sigma_y + 80)(\sigma_x + 30)} \exp\left(-\frac{y^2}{2(\sigma_y + 80)^2} - \frac{h^2}{2(\sigma_z + 30)^2}\right)$$

Where:

h = stack height

MILLER AND HOLZWORTH (1967)

$$\frac{X}{Q} = \frac{\bar{u}}{x}\left[\int_{50}^{t_H}\int_{50}^{t_H} \frac{2}{\sqrt{2\pi}\,\sigma_z}\,dt\,dt + \int_{t_H}^{t_x}\int_{t_H}^{t_x} \frac{1}{H}\,dt\,dt\right]$$

TABLE 16

CHARACTERISTICS OF ATMOSPHERIC POLLUTANT TRANSPORT PROCESSES: RECEPTOR ORIENTATED REGRESSION MODELS

MILLER (1967)

$$X = a + bQ + c\bar{u} + dH \qquad (1)$$

$$X = a + bQ + \frac{c}{\bar{u}} + \frac{d}{H} \qquad (2)$$

$$X = a + b\frac{Q}{\bar{u}H} \qquad (3)$$

Using daily data for Los Angeles and Washington, D.C., percentage of variance accounted for was as follows:

	Los Angeles (Per Cent)	Washington, D.C. (Per Cent)
Equation (1)	26	41
Equation (2)	41	62
Equation (3)	30	61

Δt: daily (146 days for Los Angeles, 58 days for Washington, D.C.)

ROBERTS AND CROKE (1968)

$$X = C_o + C_1 Q_1 + C_2 Q_2 + \sum_{i=1}^{n} k_1 Q_i$$

Where:

C_o = background level

Q_i, Q_2 = area sources

Q_i = point sources

C_1, C_2, k_i represent $\frac{1}{\sigma_y \sigma_z}$ in the Gaussian diffusion equation.

symposia on urban atmospheric modelling. Of this literature, which was mainly directed toward the meso-climatic pollution problem, only four papers were related to long distance transport modelling - Slade (1967), Johnson et al (1970), Reiquam (1970a) and Rodhe (1972). Moreover, of the models reviewed, few explicitly estimated contaminant deposition. Usually atmospheric concentration was the output parameter.

In proposing a model, we have adopted what we believe to be the best features of previous efforts, but at the same time have attempted to balance model complexity and computational requirements. Moreover, we propose to maintain simplicity in our modelling approach until additional complexity is clearly shown to be justified in terms of greater accuracy.

5.2.1 - Review of Deposition Processes

Deposition of airborne contaminants may occur by wet, dry or gaseous processes. Following basically the work of Hidy (1970 and 1971), the wet and dry processes consist of the following:

Dry

1 - Gravitational sedimentation

2 - Diffusional and inertial deposition on vegetation, structures, etc.

3 - Particle collisions

4 - Chemical reactions.

Wet

1 - Rainout from clouds:
  (a) Collision mechanisms
  (b) Phoretic mechanisms
  (c) Electrical charge

2 - Washout below clouds:
  (a) Small droplets - Brownian diffusion across streamlines
  (b) Large droplets - capture by wake eddies

3 - Chemical reactions.

As seen from the above list, deposition is the result of many complex processes. In general, it is a function of emission rate, wind speed, distance from source,elevation, particle size, atmospheric stability, particle electrical charge and precipitation intensity and duration.

The following algorithm, based on exponential decay, was developed by Makhon'ko (1967) for wet deposition:

$$C_t = \underbrace{\alpha q_o + \beta q_o e^{-\sigma_o t}}_{\text{rainout}} + \underbrace{\gamma q_o e^{-\sigma t}}_{\text{washout}}$$

Where:

C_t = contaminant concentration in rainwater at time t after start of rain

q_o = contaminant concentration in sub-cloud layer at t = o.

α, β and γ = time independent factors dependent on the meteorological conditions.

σ_o = rainout coefficient.

σ = washout coefficient.

Makhon'ko assumed q_o to be constant with elevation and, from field data, determined that:

$$\sigma = 10^{-4}\text{-}10^{-5}\ \text{sec}^{-1}$$

$$\sigma_o = 10^{-3}\text{-}10^{-4}\ \text{sec}^{-1},$$

thus indicating rainout to be the more significant process. However, Anderson (1969) showed that washout predominated if a gradient of q_o, i.e., q_o decreasing with height, existed. Other workers have obtained reasonable results by assuming only the washout portion of the equation. Recently, more sophisticated models involving raindrop kinetics have been developed; however, they still retain an exponential decay function.

Concerning dry or gaseous processes, the literature reviewed to date indicates both that these processes are more complex than is wet deposition and that research is not as advanced in these areas. Further work will be required early in Phase Two to determine a reasonable model for the dry and gaseous processes.

5.3 - The Transport Model

The transport model proposed is based on Slade's (1967) 'box' approach and, for simplicity, employs the following assumptions:

- quasi steady-state conditions during the operational unit time period.
- superposition of loadings from different sources.
- constant emission rates from a source during the operational unit time period.
- complete vertical and horizontal mixing of the pollutant within the 'box'.

Slade's model was:

$$\chi_r = \frac{Q\,D\,W}{\bar{u}\left(\frac{2\pi r}{16} + y\right)H} \qquad (1)$$

Where:

χ_r = average concentration at r

W = fractional frequency of the wind direction into 16 direction sectors

Q = emission source strength

r = distance from source to receptor

H = depth of atmosphere through which the plume is mixed

y = diameter of circle of area equal to the emission area

$\bar{u}$ = average wind speed

D = decay by various scavenging mechanisms.

Modifications, made to model the various air mass and synoptic conditions and to take into account wet and dry deposition en route from the source areas to the Upper Great Lakes, yield the following algorithm. Figure 9 illustrates the model diagrammatically.

For each wind direction sector between source and receptor,

$$\text{if } \bar{u} = 0 \qquad \chi_r = 0$$

$$\text{if } \bar{u} > 0 \qquad \chi_r = \frac{Q\ D\ L}{\bar{u}(\phi_i r + y) H_i} \tag{2}$$

Where additional variables are:

L = loss function equalling the proportion of contaminant remaining after wet and dry deposition,

ϕ = angle of dispersion,

i denotes variables which are a function of air mass type.

It follows that the horizontal flux over a given site is:

$$F = \frac{Q\ D\ L}{(\phi_i r + y) H_i} \tag{3}$$

5.3.1 - Operational Unit Time Period

It is proposed to carry out the computations on a daily basis, assuming that quasi steady-state conditions hold within the day. This will allow changes in emission rates and atmospheric stability to be modelled. In addition, from a climatological point of view, this is a suitable period as both wind and precipitation data are readily available at this time scale.

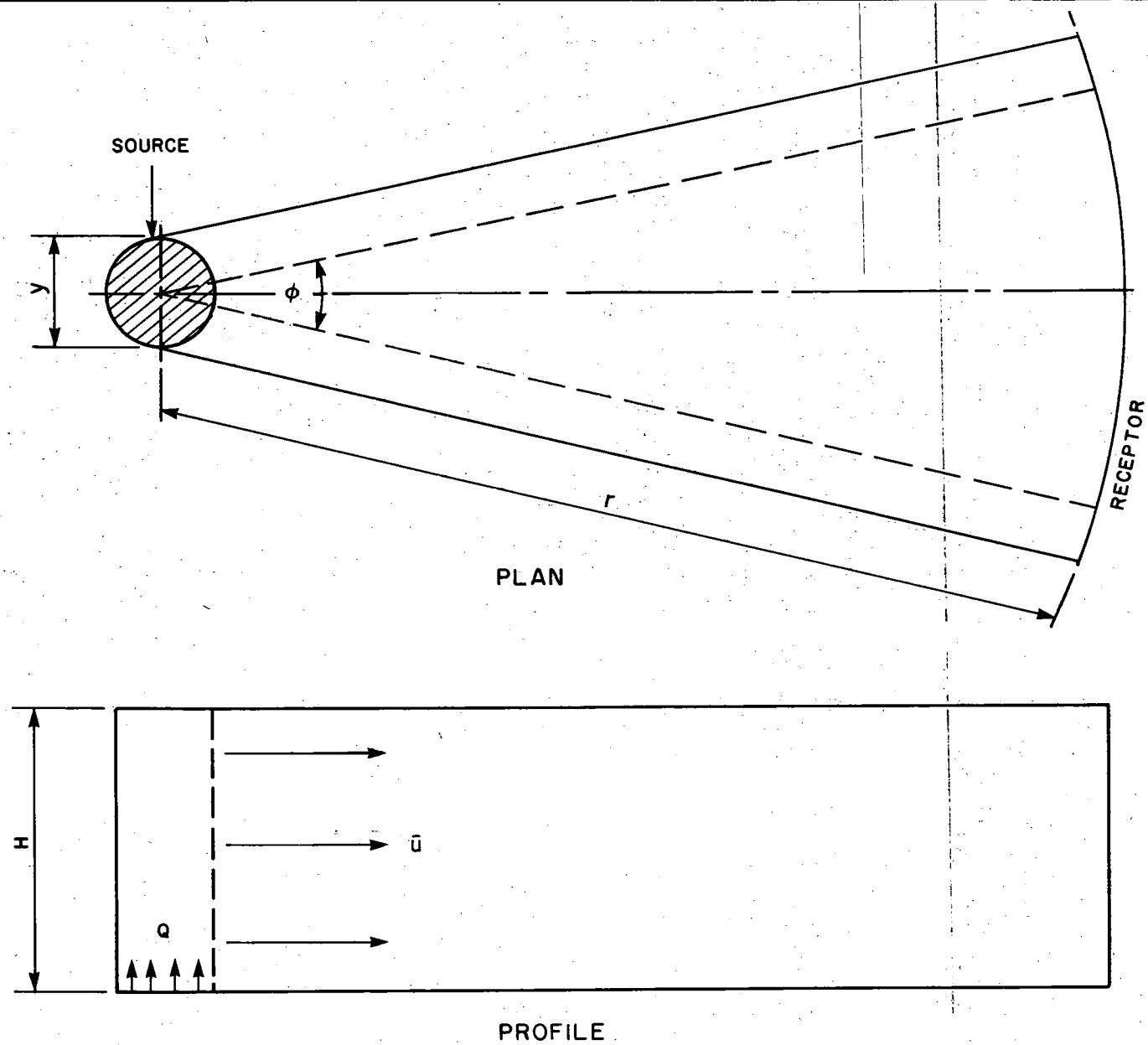

FIGURE 9

ELEMENTS OF BOX MODEL

5.3.2 - Emission Rates

Based on the emission survey, a number of point and area emissions will be recognized and average daily emissions rates, Q, and areal extent, y, will be determined. Initially, however, emission rates will be assumed to be constant throughout the year.

5.3.3 - Air Mass Type and Mixing Depths

In order to estimate the depth of the lower atmosphere through which the emissions from area sources will disperse over the relatively long transport distances, mixing depth climatologies will be developed for the following air mass types: Maritime Tropical (MT), Maritime Polar (MP), Maritime Arctic (MA) and wintertime only Continental Arctic (CA).

Preliminary estimates of seasonal variations in these mixing depths for undisturbed conditions over the Upper Lakes are as follows:

Air Mass Type	Mixing Depths in Feet			
	Winter	Spring	Summer	Fall
CA	1,750	Rare	Never	Rare
MA	2,250	2,600	3,000	2,600
MP	3,000	3,500	4,000	3,500
MT	Never	Rare	5,000	Rare

5.3.4 - Diffusion Characteristics*

The algorithm adopted to represent the transportation process allows the concentration of the contaminant in the horizontal transverse direction over the receptor to be modified with respect to the air mass

*The concept that the box angle ϕ is related only to stability was re-examined early in Phase Two, and it is now defined such that it relates to both stability and wind variability over the 24-hour operational period.

condition. For each condition, the 'box' angle ϕ is related to the distance from the source through the horizontal Pasquill-Gifford dispersion coefficient, σ_y. The angle computed is such that the spread accounts for about 95 per cent of the contaminant. Data are based on Figure 3.2 in Turner (1969). Computed angles and stability classes (as defined by Turner) are listed below for an estimated average stability in each air mass type.

Air Mass Type	Stability	ϕ
CA	D	9 degrees
MA	C	12 degrees
MP	A-B	20 degrees
MT	A	27 degrees

5.3.5 - Mean Wind Speed and Direction

It is anticipated that the wind field will be one of the most sensitive parts of the model. The field will be specified using surface and 850-mb levels in terms of direction and speed on a daily basis. Initially, it will be assumed that no more than 1 day's travel will be required to transport contaminants from source to receptor.

5.3.6 - Decay of Non-conservative Contaminants

An exponential decay based on the half-life of the contaminant will be adopted. The functional relationship will be of the form:

$$D = \exp\left(-0.693 \frac{r}{\bar{u}\, T_{1/2}}\right) \qquad (4)$$

Where:

$T_{1/2}$ = half-life of the contaminant.

5.3.7 - Wet and Dry Deposition

Initially, the algorithm to account for daily wet and dry deposition will be:

$$L = \underbrace{e^{-\lambda t}}_{wet} \underbrace{\left(\frac{24-t}{24}\right)\left(1-Dd\right)}_{dry} \tag{5}$$

Where:

L = fraction of initial concentration remaining at the end of the day

λ = scavenging coefficient

t = duration of storm(s) during the day

Dd = fraction deposited by dry deposition.

This approach assumes that wet deposition occurs as an exponential decay. The form of Dd to be used has not yet been decided upon.

Alternately, an attempt will be made to base the quantity of wet deposition on certain synoptic conditions which imply precipitation events rather than on actual records of precipitation. Whenever precipitation-producing synoptic events, such as cold or warm fronts and moving or stationary low-pressure cells, are identified, the pollutants from sources located more than 50 km (say) from the receptor will be assumed to be totally removed from the air (by wet deposition) before reaching the receptor. For sources near the lakes, it will be assumed that washout will occur within 50 km.

5.3.8 - Model Verification

To test the model, we propose comparing monthly deposition rates with values measured at the sampling

stations located around the Upper Great Lakes (Figure 1). In addition, the effect on the output of errors in the input parameters will be assessed using sensitivity analysis.

5.3.9 - Model Limitations

The proposed model is limited both by the assumptions made and limitations in field data. We list some of the major shortcomings below. It is proposed to evaluate these during the early phase of model development.

(a) The quasi steady-state assumption fixes variables within the operational time unit of 1 day. Certain variables are known to vary significantly within this period; for example, wind field and air mass/synoptic conditions. It is also possible that the 1 day period is too long with respect to the turnover time of the contaminant being modelled.

(b) The wind field is averaged on a daily basis with 45-degree sectors. No attempt is made to follow the actual trajectory.

(c) Dispersion of the contaminant is assumed to be uniform within the 'box'. Considering the travel distances involved, this is probably valid for the vertical plane, but an oversimplification in the horizontal plane. The coarse definition of the wind field and initial limitations of daily data prevent a more accurate representation. The definition of the 'box' size through ϕ and H is a crude approximation of the actual atmospheric conditions. We also assume that losses through the top of the box are negligible.

(d) Depositional processes are highly complex mechanisms, and at present inadequately understood. The simple approaches proposed here cannot be expected to accurately model the real processes.

(e) The spatial representation of climatic conditions is limited by necessity to average or weight data.

(f) The assumption of superposition may not be valid for non-conservative pollutants.

(g) A further factor that needs to be noted relates to emission data. For simplicity, it is necessary to lump and average the data at major source areas both in terms of space and time. In addition, the limited accuracy of the emissions data must be recognized.

5.4 - Multivariate Model Approach

In contrast to the theoretically based procedure outlined above, it is also proposed to relate observed monthly precipitation loading values to variables that would be expected to affect the loadings. This approach will assist in evaluating the importance (with regard to loadings) of the pseudo-independent variables, as well as providing a wholly empirical means of estimating loadings at non-gauged locations. Initially, a step-wise multiple regression analysis will be carried out, using all available monthly precipitation chemistry data. The independent variables to be considered will include the following:

- loading site location	- latitude and departures
- monthly wind	- frequency of direction and speed
- precipitation	- monthly depth, precipitation days
- air mass	- frequency of four types
- synoptic condition	- frequency of eight types.

For those chemical loading values where sufficient data are available, parameters will be estimated from half the data, the remainder being used to test the validity of the relationships.

5.5 - Bibliography for Section 5

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6 - CONCLUSIONS

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6.1 - Sources

Based on emissions data, eight primary source areas have been identified and 1973 values determined for particulates, oxides of sulphur and nitrogen, hydrocarbons and carbon monoxide. In addition, the amount of fringe area emissions has been delineated.

The data show that total emissions from the primary sources around the Upper Great Lakes are as follows:

Particulates	-	3.0 million tons per year
SO_x	-	8.3
NO_x	-	5.1
Hydrocarbons	-	3.1
CO	-	12.7

Chicago-Gary and Detroit-Windsor-Cleveland industrial regions, which account for 30 per cent and 33 per cent respectively of the primary source emissions, are the main emission areas; the Toronto-Hamilton area emitting 15 per cent is also significant. The Sudbury area is the main source of SO_x (yielding 32 per cent of the primary sources).

6.2 - Precipitation Chemistry Analysis

(a) Data are lognormally distributed. In view of this, logarithmic transforms should be carried out on all data before they are statistically analyzed.

(b) Factor analysis of the monthly precipitation concentration data shows a strong industrial factor defined by heavy metals, sulphate, and nitrate, a marine incursion factor defined by Cl and Br, a smelter factor defined by total Ni and Cw, and an agricultural factor defined by various combinations of phosphorus, sulphate, nitrate, ammonia, and alkali-alkali metals.

(c) Comparison of CCIW and McMaster data reveals that:

(i) For the idential parameter, loading data are reproducible to within about 50 per cent. This reproducibility includes the effect of different sampler designs.

(ii) The heated rain sampler design of CCIW is less efficient than the Alter Shield snow collector of McMaster.

(iii) The exact sample preparation, especially with regard to filtering, affects differences of up to 1,000 per cent.

(d) There is no significant difference between monthly concentration data collected onshore and individual event samples collected on ship after inconsistently high data are first removed.

6.3 - Loadings

Tentative estimates of yearly loadings are as follows:

	Lake Superior (tons/year)	Lake Huron (tons/year)
T PO_4	7,000	5,000 as PO_4
NO_3	50,000	70,000 as N
SiO_2	70,000	100,000
Alk	330,000	310,000 as $CaCO_3$
Cu T	400	550
Pb T	700	740
Ni T	160	200
Zn T	6,000	5,000
SO_4	300,000	310,000

6.4 - Modelling

The literature reveals that few models have been developed which simulate atmospheric pollutant transport over long distances. Moreover, most of the models deal with estimating atmospheric concentrations rather than surface loadings of pollutant. Our review indicates that,initially,a 'box' type model should be developed using daily meteorologic data. A simple approach will be maintained until additional complexity is clearly shown to be justified in terms of greater accuracy.