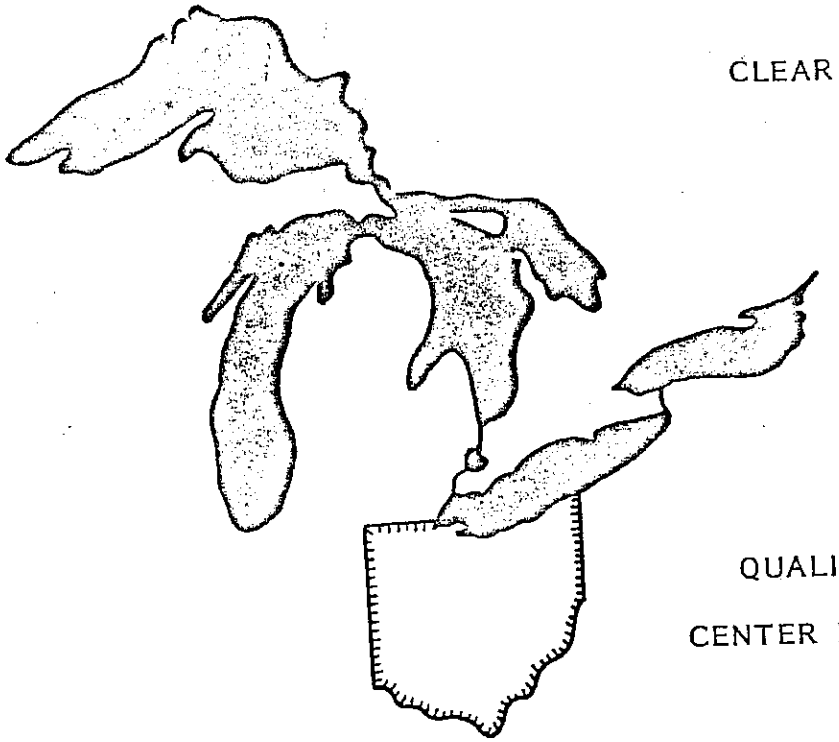


CLEAR TECHNICAL REPORT NO. 275

QUALITY ASSURANCE PROJECT PLAN FOR THE CENTER FOR LAKE ERIE AREA RESEARCH

Prepared by

Laura A. Fay

Prepared for

U.S. Environmental Protection Agency
Great Lakes National Program Office
Chicago, Illinois

THE OHIO STATE UNIVERSITY
CENTER FOR LAKE ERIE AREA RESEARCH
COLUMBUS, OHIO

April 1983

PREFACE

The format of the quality assurance plan that follows is slightly awkward and repetitious. The design of the 16-section plan is in direct response to guidelines established by the U.S. Environmental Protection Agency's Quality Control Office. The meat of the plan can be found in section 11. Detailed information on our standard operating field and laboratory procedures can be found in CLEAR Technical Report no. 205 (Letterhos 1982).

1. QA Project Plan

for the

Center for Lake Erie Area Research

Project Manager

QA Officer

Laboratory Director

USEPA Project Officer

USEPA QA Officer

INTRODUCTION

All components of the proposed Lake Erie Studies will be subjected to the quality assurance system designed by CLEAR. In addition to the in-house QC program CLEAR also participates in IJC round robins and USEPA Performance Evaluations (PE's). On a tertiary level, QC samples solicited from the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati are analyzed. CLEAR acknowledges the right of the sponsor to conduct on-site quality assurance system audits at any time. CLEAR also wishes to express a willingness to participate in any Performance Evaluation studies that are appropriate. A detailed description of our Quality Control and Assurance Plan for Lake Erie Studies follows.

Section 2

TABLE OF CONTENTS

Section No. 1
Revision No. 1
Date April 22, 1983
Page 3 of 13

Section #		Page
	Introduction	2
3	Project Descriptions	3
4	Project Organization and Responsibility	4
5	QA Objectives for Measurement Data in terms of Precision, Accuracy, Completeness, Representativeness and Compatability	6
6	Sampling Procedures	6
7	Sample Custody	7
8	Calibration Procedures and Frequency	7
9	Analytical Procedures	8
10	Data Reduction, Validation and Reporting	8
11	Internal Quality Control Checks	8
12	Performance and System Audits	11
13	Preventative Maintenance	11
14	Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness	11
15	Corrective Action	12
16	Quality Assurance Reports to Management	13
	Appendix A - Standard Operating Procedure (Letterhos 1982)	
	Recipients of CLEAR's QA Project Plan	
	a. Quality Assurance Office	
	b. International Joint Commission	
	c. David Rockwell (USEPA-GLNPO)	

3. PROJECT DESCRIPTIONS

Open Lake Stratification Study

This project will begin in early June and end in late August 1983. The main objective will be to calculate the volumetric oxygen depletion rate for the central basin of Lake Erie. The parameters to be sampled include oxygen, total phosphorus, soluble reactive phosphorus, and chlorophyll a. In addition, temperature profiles will be taken at all stations.

Harbor Contaminant Study

This project will span the spring, summer and fall (one cruise each season) in order to cover all levels of tributary flows. The main objective of this study is to update the information available on the contaminants associated with specific harbors within a timely interval. Samples will be collected for the standard limnological parameters plus several toxic metals, and polynuclear aromatic hydrocarbons (PAH) for water, particulates and several biological components.

Ashtabula Harbor Dredging Study

This project will closely bracket the dredging activity to be undertaken in late July or early August in Ashtabula Harbor. The objective will be to determine the effects of dredging activity on the adjacent areas and to monitor the mobilization of metals from the sediment.

Cladophora Surveillance Study

This project will monitor the nutrient uptake, growth rate, density and distribution of the filamentous alga, Cladophora at a western, central and eastern basin site. Physical, chemical and Cladophora biomass data will be collected bimonthly from mid-May through October 1983 to 1985.

4. PROJECT ORGANIZATION AND RESPONSIBILITY

1. The principal investigator is ultimately accountable for the completion of the report and the validity of all the data. The final

report prepared by the PI will describe the QC efforts throughout the project and present a table summarizing the accuracy and precision of all parameters (Figure 1).

2. The Quality Assurance Officer (QAO) is responsible for establishing the QC sampling strategy for a specific program and ensuring that it is carried out. The QAO is responsible for reviewing all the QC data and evaluating the results. The QAO is also responsible for responding to PE audits and IJC round robins (Figure 1).

3. The Chief Scientist of Field Operations is responsible for the field collection of Quality Control samples as well as an immediate overview of QC information collected on board the vessel for physical and dissolved nutrient parameters. The Chief Scientist oversees the preparation of the resulting QC file for computer entry.

4. The Laboratory Director has the responsibility of supervising the analysis of total nutrients, particulates, metals and daily quality control. An added duty is the supervision of the computerization of the data and QC files (Figure 1).

5. QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, RESPRESENTATIVENESS AND COMPARABILITY

TABLE 1

QUALITY CONTROL SUMMARY FOR 1982

	Std. Dev.*	Range Limit	Scale and/or Units	N	% of Samples Within Range Limits
Chlorophyll a Corrected	0.31	1.2	ug/l	64	95.3
Conductivity Corrected to 25°C	2.12	7.8	umhos/cm	64	96.1
Dissolved Oxygen	0.06	.2	mg/l	58	96.6
pH	0.018	.07	units	64	98.4
Temperature	0.06	.2	°C	50	96.4
Transparency (Secchi)	0.12	0.4	Meters	35	91.4
Turbidity	0.39	1.4	ntu's	64	95.3
Ammonia	1.16	4.3	0-100 ug/l	127	95.3
Nitrate + Nitrite	0.0020	0.007	0-1 mg/l	130	91.5
Soluble Reactive Phosph.	0.23	0.8	0-50 ug/l	129	95.3
Total Phosphorus	0.32	1.2	0-100 ug/l	130	96.1
Total Filtered Phosphorus	0.33	1.2	0-50 ug/l	130	96.9
Soluble Reactive Silica	0.007	0.03	0-5 mg/l	130	95.0

*Standard Deviations are calcuated using the system authorized by the IJC

6. FIELD SAMPLING PROCEDURES

1. The types of sample containers to be utilized during this project are highlighted in Table 2. Details of the standard operating procedures (SOP) are available in Letterhos 1982.

2. Samples will be identified by station number, Julian sampling date and depth of collection. A log book will be maintained of all samples.

3. Field data will be recorded on a station by station basis. A field log will be updated daily to include number of stations, personnel, meteorological observations, problems in field analysis and laboratory analysis performed.

4. Samples received in the laboratory will be checked against the daily field summary sheets. Log books will also be kept on a parameter by parameter basis.

5. Field and laboratory methods are summarized in Table 3. Details of these methods and their references can be obtained from Letterhos, 1982.

6. Detection limits are also presented in Table 3.

7. Variances from Standard Methods/EPA procedures:
The forms of phosphorus requested will be analyzed by the stannous chloride not the absorbic acid technique. This variance has been allowed since 1974.

7. SAMPLE CUSTODY

The custody of samples is reflected in the flow chart of project organization and responsibility (Figure 1). A description of sample logging procedures is briefly described in section 6. The type of samples received and analyzed by CLEAR do not presently require this type of security.

8. CALIBRATION PROCEDURES AND FREQUENCY

Intervals between calibration of different pieces of field equipment are unique to the specific instrument. The interval is based on the history of the instrument, desired precision/accuracy and its stability. Details of calibration methods are available (Letterhos 1982). All field equipment is calibrated daily and receives preventative maintenance prior to each cruise.

9. ANALYTICAL PROCEDURES

A table summarizing the methods and detection limits is included in this plan (Table 3). For details of our standard operating procedures please refer to Letterhos 1982.

10. DATA REDUCTION, VALIDATION AND REPORTING

Information regarding calculations performed on raw data is presented along with the other necessary information of detection limits, precision and accuracy for individual parameters in the SOP manual (Letterhos 1982).

11. INTERNAL QUALITY CONTROL CHECKS

General Water Sampling Procedure

1. All water samples are obtained by a submersible pump or Niskin bottle. When collecting replicate samples, two separate casts are made and labeled as $O1_1$, $O1_2$ and/or B_1 and B_2. Sufficient pumping time is allowed to clear the line of any previous sample before collecting new samples (O1 - surface, B - bottom).

2. A split, as referred to in the following procedures, indicates a sample run twice from the same cast (i.e., $O1_1$ → Split Split; $O1_2$ → Split Split)

Auto Analyzer QC

This program is more extensive than outlined for other parameters. This is because of the number of potential variables involved in the determination of concentrations plus the analytical procedures utilized for the analysis are more conducive to running replicates and splits.

1. A replicate sample is taken at every QC station ($O1_1$, $O1_2$ etc.)

2. Every replicate sample is analyzed twice as separate runs. This is a split making a total of four values for each QC sampling depth.

3. Replicates and splits are recorded in the QC logbook and the difference between splits (within cast replicate) is calculated as the range.

4. Replicate samples at each QC station ($O1_1$, $O1_2$, B_1, B_2) are spiked with a known standard concentration in a 1:1 ratio (usually 4 ml sample + 4 ml standard mixed in a test tube). These results are used to calculate percent recovery which gives an indication of the accuracy of the method.

$$\% \text{ recovery} = \frac{\text{actual spiked value}}{\text{theoretical value}} \times 100$$

$$\text{Theoretical Value} = \frac{\text{Spiking standard + Original Value of Sample}}{2}$$

Actual Spike = Read off chart

All of these values are recorded in the AA QC logbook.

Estimating Standard Deviations (IJC Procedure)

1. Add ranges derived from differences in the splits and calculate the mean. Discard any ranges that differ significantly from the majority.

2. Divide the mean by 1.128 to obtain standard deviations.

3. Control limits are determined by multiplying the estimated standard deviation by 3.686. Whenever a range falls out of the boundaries of this limit, the system is said to be out of control.

4. To pool estimates of standard deviations use the following equation.

$$S^2 = \frac{(n_1-1)\ (S_1^{\ 2}) \ + \ (n_2-1)\ (S_2^{\ 2})}{(n_1-1) \ + \ (n_2-1)}$$

n_1 = number of values in first set
S_1 = standard deviation of first set
n_2 = number of values in second set
S_2 = standard deviation of second set

QC Program for Particulates (Chlorophylls, Suspended Solids, POC, PON and Turbidity)

1. An identical aliquot is filtered from each replicate cast ($O1_1$, $O1_2$ and B_1, B_2).

2. A split is filtered from only one of the replicate casts at each QC station and labeled as a split (i.e., $O1_1$ split). There will be 3 QC samples from the O1 depth ($O1_1$, $O1_2$ and $O1_1$ split).

QC Program for All Remaining Parameters

1. Replicate samples are taken wherever possible (DO, alkalinity, conductivity and pH).

2. Splits are done for conductivity and pH when using YSI and Orion meters.

3. Replicate EBT traces are taken from surface to bottom at QC stations. When applicable, replicate readings are taken for conductivity and pH.

4. Secchi and extinction depth replicate values are recorded by two individuals.

Selection of QC Stations

1. Selection is random and one station is picked each morning prior to arriving at the first station.

2. If stratification exists, quality control sampling is done at surface and bottom depths. When the water column is unstratified QC is done only at one depth.

   Differences between pairs greater than the control limits (previously determined 1980-1983) used to determine "out-of-control" situations. Since this analysis is conducted on a daily basis, the operator can check for chemical, electrical and mechanical problems before rerunning samples.

12. PERFORMANCE AND SYSTEM AUDITS

1. IJC Round Robin samples are periodically analyzed for selected parameters and compared with results of other laboratories. CLEAR has participated in the IJC program since 1978.

2. Known sample concentrations provided by the EPA are analyzed periodically. These samples are solicited from the EMSL laboratory in Cincinnati and run annually or bi-annually.

3. Performance Evaluations Samples (PE's) distributed by the USEPA have been analyzed when provided.

13. PREVENTATIVE MAINTENANCE

Each operator is familiar with their associated instrument and is able to anticipate many maintenance problems. Each piece of field equipment is checked and calibrated prior to each cruise. In many cases, duplicate pieces of equipment are carried on board as backup instruments. The only insurmountable problem is down time due to boat problems (i.e. engine or generator breakdown).

14. SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

A computer program is currently available to evaluate quality control information on a cruise and/or annual basis. A histogram is plotted of the differences of within and between cast duplicates. Normal and non-parametric statistics are provided for each parameter. Recovery data based on spikes for nutrient parameters is also generated by computer program.

A step-by-step view of QC analysis from data entry to the ultimate determination of precision and accuracy follows:

Transfer of QC data into the Data Management File

1. Stations are entered in order sampled, cruise by cruise.

2. QC sampling procedures at individual stations will follow set pattern (i.e., QC will be done at the same stations both on the Hydra and in Columbus).

3. The following codes will be used when transferring data.

QC Code	Value
11	replicate 1, split 1 ($O1_1$ value 1)
12	replicate 1, split 2 ($O1_1$ value 2)
21	replicate 2, split 1 ($O1_2$ value 1)
22	replicate 2, split 2 ($O1_2$ value 2)
81	original value ($O1_1$) before spiking
82	observed value of spike
83	spike standard
84	volume of sample
85	volume of spike if ratio is different than 1:1
91	original value ($O1_2$) before spiking
92	observed value of spike
93	spike standard
94	volume of sample
95	volume of spike if ratio is different than 1:1

4. Data should always be entered in the above order (not including 84, 85, 94 and 95), entering N if no data exists.

5. Two Data Management data sheets are available, one for parameters analyzed in Columbus and one for parameters analyzed aboard the R/V Hydra. The order of entries should be identical.

6. Any QC data run which is above and beyond that required, or is just different from the set pattern, should be entered at the end of each cruise interval.

15. CORRECTIVE ACTION

Corrective Action is invoked when the difference between duplicates exceeds the predetermined limit established by the calculations of the

existing QC data base. A listing of these corrective action values is presented in Table 1, section 5. Based on the magnitude of the discrepancy there are two levels of action.

1. Both duplicate samples can be rerun and their differences recalculated.

2. The system's calibration would be rechecked with an array of standards and blanks run. If the system still failed to comply troubleshooting procedures would begin.

16. QUALITY ASSURANCE REPORTS TO MANAGEMENT

Reports on the data precision and accuracy are provided to the principle investigator(s) and sponsors on an annual basis, accompanying the data report. The Quality Control officer is responsible for the timely completion of this report. One example from the quality control management report for 1982 is provided (Table 4).

FIGURE 1

PROJECT ORGANIZATION AND RESPONSIBILITY

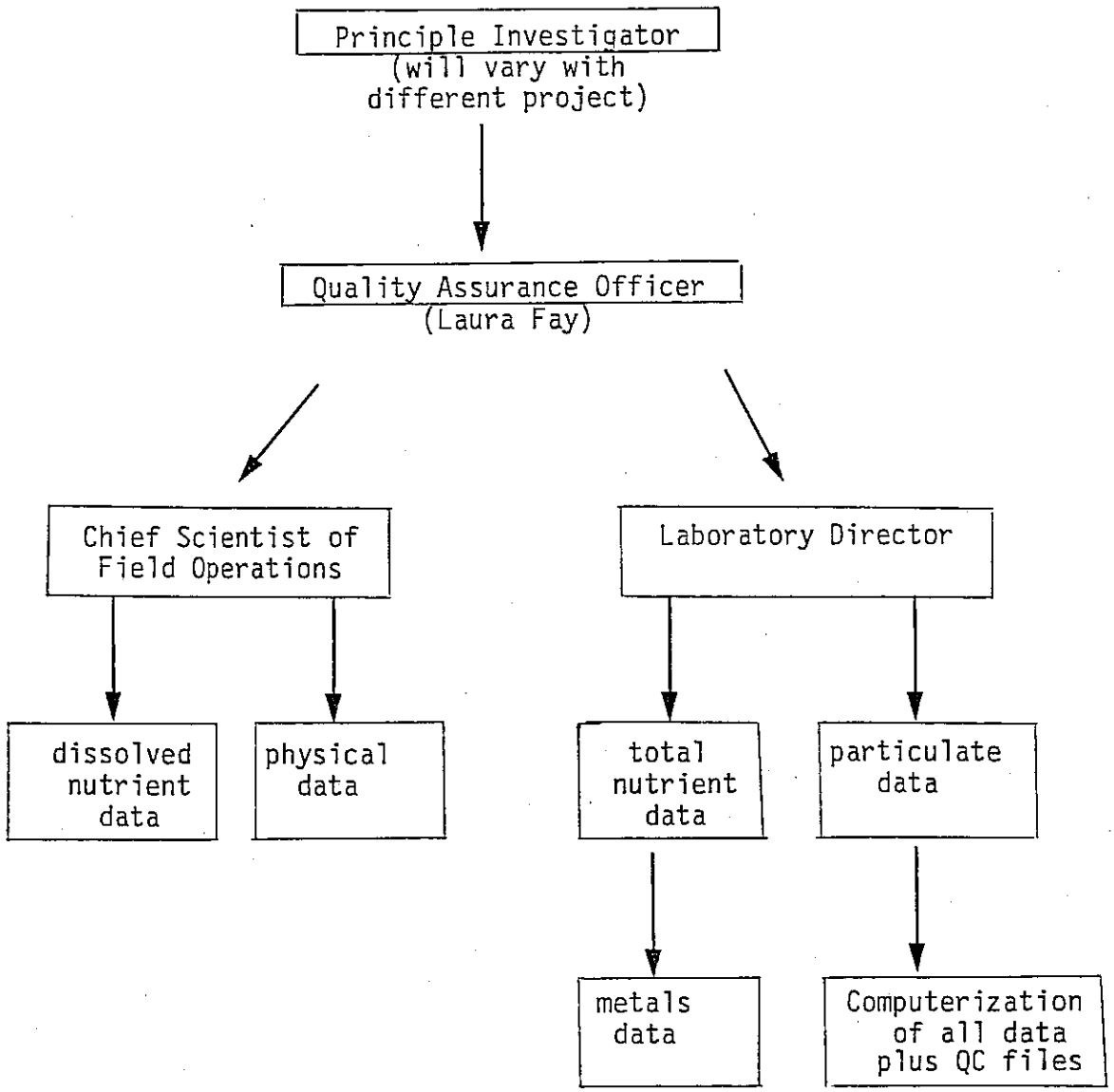


TABLE 2

SAMPLE CONTAINERS AND PRESERVATION FOR LAKE ERIE SAMPLES

Parameter	Container	Preservative	Storage Time
Arsenic, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Cadmium, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Chromium, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Copper, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Iron, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Lead, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Lead, D	poly	Ultrapure HNO_3 to pH less than 2	6 months
Manganese, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Mercury, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Nickel, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Selenium, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Silver, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Zinc, T	poly	Ultrapure HNO_3 to pH less than 2	6 months
Specific Conductance	poly	cool, 4^oC	24 hrs.
Dissolved Oxygen	glass 300 ml BOD	fix on site	none
pH	poly	none	6 hrs.
Turbidity	poly	cool, 4^oC	7 days
Suspended Solids	plastic petri dish	filter thru GF/C; desiccate	1 month
Color	poly	cool, 4^oC	24 hrs.
NO_3+NO_2, Nitrogen	poly	cool, 4^oC	24 hrs.
Ammonia, Nitrogen	poly	cool, 4^oC	24 hrs.
Kjeldahl, Total Nitrogen	glass	freeze	6 months
Total Phosphorus	glass	cool	1 month
Total Filtered Phos.	glass	cool	1 month
Soluble Reactive Phos.	poly	cool, 4^oC	24 hrs.

TABLE 2 CONT.

SAMPLE CONTAINERS AND PRESERVATION FOR LAKE ERIE SAMPLES

Parameter	Container	Preservative	Storage Time
Carbon, Organic Diss.	glass	cool, 4°C, HCl to pH less than 2	1 month
Alkalinity	poly	cool, 4°C	24 hrs.
Chloride	poly	cool, 4°C	1 month
Sulfate	poly	cool, 4°C	1 month
Total Coliforms	sterilized glass	cool, 4°C during transport	none
Fecal Coliforms	sterilized glass	cool, 4°C during transport	none
Phytoplankton	poly	cool, 4°C during transport	none
Chlorophyll	plastic petri dish	filter on GF/C; add $MgCO_3$; freeze	6 months

TABLE 3. SYNOPSIS OF METHODS FOR LAKE ERIE STUDIES

Parameter	STORET Code	Method	Detection Limit
Arsenic, T	01002	HGA	25 (ug/l)
Cadmium, T	01027	HGA	5 (ug/l)
Chromium, T	01034	flame	25 (ug/l)
Copper, T	01042	HGA	10 (ug/l)
Iron, T	01045	flame	150 (ug/l)
Lead, T	01051	HGA	5 (ug/l)
Lead, D*	01049	HGA	5 (ug/l)
Manganese, T	01055	HGA	25 (ug/l)
Mercury, T	71900	cold vapor	0.2 (ug/l)
Nickel, T	01067	HGA	3.0 (ug/l)
Selenium, T	01147	HGA	2.0 (ug/l)
Silver, T	01077	HGA	0.5 (ug/l)
Zinc, T	01092	HGA	25 (ug/l)
Temperature	00010	Thermistor (InterOcean, Martek)	0.2 °C
		Mechanical Bathythermograph	
		NBS Calibrated Thermometer	
		Reversing Thermometer	
Dissolved Oxygen	00300	Electrode (InterOcean, Martek)	
		Titrimetric (Winkler azide modification)	0.05 mg O_2/l
pH	00400	Electrode (InterOcean, Martek, Orion)	0.1
Specific Conductance	00095	In situ probe (InterOcean, Martek)	0.02 umhos
		Electrode (Beckman, YSI)	1%
Transparency	00035	Secchi disk	0.01 m
Bottom Depth	00066	In-situ depth probe (InterOcean)	0.1 m
		In-situ depth probe (Martek)	0.25 m

TABLE 3 CONTINUED

SYNOPSIS OF METHODS FOR LAKE ERIE STUDIES

Parameter	STORET Code	Method	Detection Limit
Extinction Depth	00204	Licor Quantum/Radiometer/Photometer	0.1 m
		Protomatic submarine photometer	0.1 m
Turbidity	00076	Hach Turbidimeters (Model 2100A and Ratio)	0.02 NTU
Suspended Solids	00530	Gravimetric, using Whatman GF/C glass fiber filters	0.01 mg
Color	00080	Chloroplatinate	0.25 Cl Pt
Nitrate + Nitrite	00630	Cadmium Reduction, AAII	0.005 mg/l
Ammonia	00608	Phenate Method, AAII	0.5 ug/l
			1.0 ug/l
			2.0 ug/l
Total Inorganic N	00592	By calculation	mg/l
Kjeldahl Nitrogen			
dissolved	00623	Continuous Helix Digestion with H_2SO_4	10 ug/l
total	00625	and Hydrogen Peroxide	
Total Organic N	00605	By calculation	mg/l
Total Nitrogen	00600	By calculation	0.5 ug/l
Total Phosphorus	00665	Persulfate Digestion, Stannous Chloride	0.5 ug/l
			1.0 ug/l
Total Filtered Phosphorus	00666	Persulfate Digestion, Stannous Chloride, AAII	0.5 ug/l
Soluble Reactive Phosphorus	00671	Stannous Chloride, AAII	0.5 ug/l
Total Organic Carbon	00680	Variance, by calculation	0.2 mg/l
Dissolved Organic Carbon	00681	UV Digestion - Phenolphthalein, AAII	0.2 mg/l
Alkalinity	00410	Titrimetric (.02N HCl)	0.5 mg/l
Chloride	00940	Ferricyanide, AAII	0.5 mg/l

TABLE 3 CONTINUED

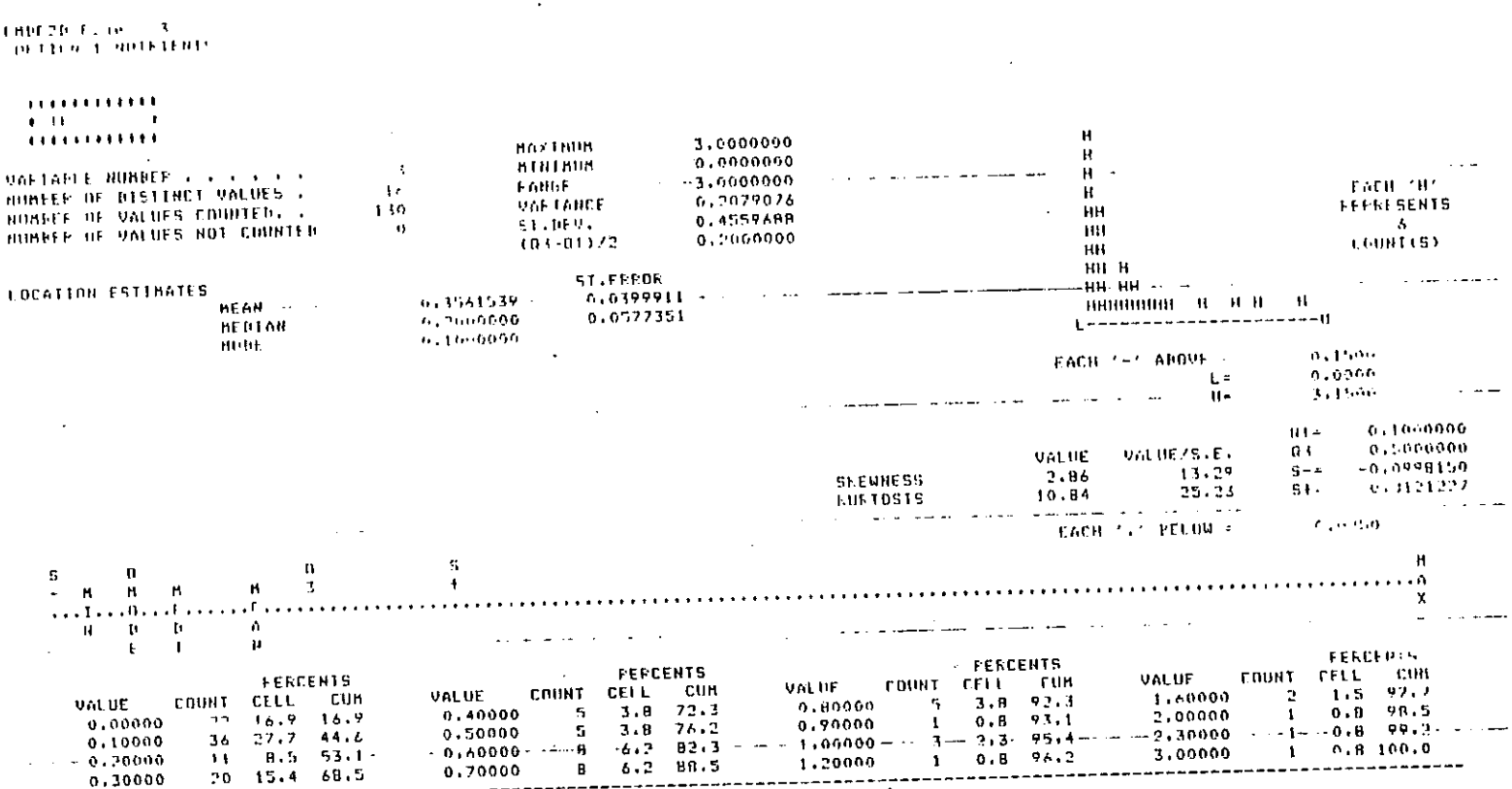
SYNOPSIS OF METHODS FOR LAKE ERIE STUDIES

Parameter	STORET Code	Method	Detection Limit
Sulfate	00945	Methylthymol Blue, AAII	0.5 mg/l
Total Coliform	31501	Membrane filtration method Standard Methods, Sect. 408A immediate	
Fecal Coliform	31616	Membrane filtration method Standard Methods, Sect. 408C	
Phytoplankton	NA	Optical examination (Collected w/ Niskin Bottle, Preserve w/Lugols)	species
Chlorophyll a corrected	32211	Acetone extinction Varian Spectrophotometer	0.02 ug/l
Pheopigment	32218	Acetone extinction Varian Spectrophotometer	0.04 ug/l

T = total
D = dissolved
* Dissolved fraction will only be analyzed if total lead exceeds 30 ug/l.

Table 4

Total Phosphorus Quality Control Report to Management



VARIABLE NUMBER	3	MAXIMUM	3.0000000
NUMBER OF DISTINCT VALUES	12	MINIMUM	0.0000000
NUMBER OF VALUES COUNTED	130	RANGE	-3.0000000
NUMBER OF VALUES NOT COUNTED	0	VARIANCE	0.2079076
		ST.DEV.	0.4559488
		(Q3-Q1)/2	0.2000000

LOCATION ESTIMATES

	MEAN	ST.ERROR
MEAN	0.3561539	0.0399911
MEDIAN	0.2000000	0.0577351
MODE	0.1000000	

EACH 'H' REPRESENTS 4 COUNT(S)

EACH '-' ABOVE = 0.1500
L= 0.0000
U= 3.1500

	VALUE	VALUE/S.E.
SKEWNESS	2.86	13.29
KURTOSIS	10.84	25.23

U1= 0.1000000
Q1 0.1000000
S= -0.0998150
S1= 0.0121227

EACH '.' BELOW = 0.0150

VALUE	COUNT	PERCENTS CELL	CUM	VALUE	COUNT	PERCENTS CELL	CUM	VALUE	COUNT	PERCENTS CELL	CUM	VALUE	COUNT	PERCENTS CELL	CUM
0.00000	22	16.9	16.9	0.40000	5	3.8	72.3	0.80000	5	3.8	92.3	1.60000	2	1.5	97.7
0.10000	36	27.7	44.6	0.50000	5	3.8	76.2	0.90000	1	0.8	93.1	2.00000	1	0.8	98.5
0.20000	11	8.5	53.1	0.60000	8	6.2	82.3	1.00000	3	2.3	95.4	2.30000	1	0.8	99.2
0.30000	20	15.4	68.5	0.70000	8	6.2	88.5	1.20000	1	0.8	96.2	3.00000	1	0.8	100.0

$$\text{Std Deviation}^* = \frac{\text{mean of differences}}{1.128}$$

$$= \frac{.356}{1.128} = .316$$

$$\text{Range}^{**} = \text{mean of differences} \times 3.268 \text{ or calc std dev} \times 3.686$$

$$.356 \times 3.268 \text{ or } .316 \times 3.686$$

$$1.16 = 1.16$$

* Std Deviation is calculated according to IJC directives

** The factor 3.268 is the ratio of 3.686/1.128

Based on the range calculated for 1982 QC data, of 1.2, 5 out of 130 pairs exceeded the limit (4%)