

# **DATA QUALITY ASSURANCE FOR WATERSHED AND LAND USE STUDIES**

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## **DISCLAIMER**

The study discussed in this document was carried out as part of the efforts of the Pollution from Land Use Activities Reference Group, an organization of the International Joint Commission, established under the Canada-United States Great Lakes Water Quality Agreement of 1972. Findings and conclusions are those of the investigators and do not necessarily reflect the views of the Reference Group or its recommendations to the International Joint Commission.



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## SUMMARY

To ensure adequate quality control within its studies, a number of actions were taken by the principal investigators and others of PLUARG Watershed Studies. The first action taken for sample quality control was to develop a quality control handbook that described the necessary protocols to determine if sampling, sample handling, and sample analysis produced data of the necessary integrity to support specific study conclusions. In addition, the protocols called for remedial actions when a laboratory was found to perform inadequately.

Subsequently, to meet the sample quality control protocols a quality assurance program was instituted. It was comprised of interlaboratory analytical performance tests, blind replicate precision tests, and the documentation of analytical methods and intralaboratory quality control procedures.

Fifteen interlaboratory analytical performance studies were conducted for nutrients, demand, minerals, metals, and pesticides in water; and for metals, nutrients, and pesticides in sediments. In addition, similar ancillary studies were carried out by several Canadian laboratories.

Several hundred blind field replicate samples were taken and analyzed. Data from these replicates were reviewed by Principal Investigators and staff of the IJC Great Lakes Regional Office.

Each participating laboratory produced descriptions of its analytical methods and "in-house" quality control procedures.

All data and documentation derived from the program were assembled by and are archived at the IJC Regional Office, Windsor, Ontario.

Almost all laboratories generated analytical data which were suitably compatible with other laboratories. The larger laboratories, who generated the bulk of the data, uniformly demonstrated the best compatibility. Most laboratories consistently demonstrated adequate recoveries on reference and spike materials in samples, and when a difficulty was found, remedial action was taken.

The analyses of the blind field replicate samples demonstrated that sampling and analytical integrity had been adequately maintained to provide useful data for PLUARG Studies.

From all the various studies in the Quality Assurance Program, only two laboratories demonstrated analytical difficulties much of the time. Appropriate steps were taken to ensure that the findings from the studies supported by these laboratories did not affect the conclusions of the Task C Work Group.

## CONCLUSIONS

The Quality Assurance Program was able to demonstrate that overall, laboratories were able to produce analytical data which were adequate for the PLUARG Task C Watershed studies. The Program was successful in removing identified analytical difficulties in all but two laboratories. Appropriate steps were taken to ensure that data derived from the two laboratories did not affect the conclusions of the Task C Work Group.

The Program established that sampling procedures, sample handling, and analyses were in control by use of field sample replicates (unidentified to the laboratory). Only five (5) percent of the replicate results were not within acceptable ranges.

The Program confirmed that laboratories producing the most data for the Watershed Studies also produced the most compatible data.

## INTRODUCTION

A number of actions were taken in an attempt to assure valid data in the PLUARG Pilot Watershed Studies. Among these actions were:

- reference samples were provided to participating laboratories;
- a replicate sample program was started;
- documentation of Sample Handling and Analytical Methods (on file in IJC Regional Office);
- meetings of Analysts and Data Handlers were held;
- preparation and Distribution of a Quality Control Handbook for Pilot Watershed Studies (QCH/PWS).

### QUALITY CONTROL HANDBOOK FOR PILOT WATERSHED STUDIES (QCH/PWS)

The QCH/PWS was developed under the leadership of the PLUARG River Basin Studies Coordinator, Dr. Darnell M. Whitt. A number of meetings and workshops was held with PLUARG members, Task C Technical Committee investigators, analysts, data handlers and invited experts in the course of handbook development. A listing of principal meetings and their purposes follows. The Handbook was approved by the Task C Technical Committee on November 4, 1976 and by PLUARG on December 1, 1976. The Handbook has since been widely circulated, and, additional copies are available from the IJC Great Lakes Regional Office.

A workshop was convened July 16-17, 1974, in East Lansing, Michigan. Attendees included Task C Technical Committee members, invited experts, and representatives of PLUARG. The objective of the workshop was to discuss methodologies employed by the various groups involved in the Task C Studies, and recommend acceptable or standardized methods to ensure that data collection, analysis and storage would be consistent and compatible among study participants.

Subgroups were established to consider the following broad areas:

- Subgroup 1. Monitoring network design, location of sampling stations, sampling techniques.
- Subgroup 2. Analytical methodologies for soil, sediment and water.

- Subgroup 3. Development of Inter- and Intra-Laboratory Quality Control.
- Subgroup 4. Data handling.

A draft report was prepared summarizing the deliberations and recommendations of each subgroup. These drafts were sent to all members of PLUARG, all members of Task C Technical Committee and to all attendees at the Workshop. Each recipient was asked to provide comments on the recommendations in the draft reports.

A second workshop was held in Madison, Wisconsin on December 3, 1974. At that meeting, the Task C Technical Committee heard reports from the 4 Subgroups. The reports covered the Subgroup recommendations, some of which were modified as a result of comments received on the draft reports of the previous meeting. The Technical Committee approved the recommendations as presented by the Subgroup Chairmen.

Concurrent with the above activities, the participating Canadian Laboratories were holding meetings on data quality.

The Task C Technical Committee at its January 21-22, 1975 meeting asked Dr. Whitt, Mr. Don King, Ontario Ministry of the Environment, and Mr. Douglas Dube, Wisconsin State Laboratory of Hygiene, to encourage the analysts toward consensus on analytical methods for soil and sediment analyses.

At its meeting January 23-24, 1975, PLUARG heard a report that intercomparisons between laboratories in Canada were underway. Mr. Dube and Dr. Whitt were asked to coordinate the work of the U.S. laboratories with the Canadian program.

On March 25-26, 1975, Messrs. King, and Dube, Dr. John Clark, IJC Great Lakes Regional Office Statistician, and Dr. Whitt met in Madison, Wisconsin. Their charge from Task C was to "refine Task C analytical control program and prepare recommendations for implementing such a program." Assistance was provided by Dr. John Konrad, Co-Chairman of Task C, and Dr. David Armstrong, University of Wisconsin. The cover sheet for the draft developed at Madison follows:

## **GUIDELINES**

### QUALITY CONTROL -- TASK GROUP C, PLUARG

This draft of "Guidelines" was prepared at the direction of the International Reference Group on Great Lakes Pollution from Land Use Activities (PLUARG), International Joint Commission, and the Task Group C Co-Chairmen of PLUARG.

Coordination of United States and Canadian Laboratory Analyses has been considered under five headings as follows:

- I. Blind Replicates from Field to Laboratories

- II. Reference and Natural Samples for Between-Laboratory Comparisons
- III. Documentation of Methodology
- IV. In-Laboratory Quality Control
- V. Data Assessment.

Copies of the "GUIDELINES" were sent to participating laboratory personnel, Task C investigators and Task C Technical Committee members. Their suggestions were requested by April 30, 1975.

The special problems associated with sediment analyses were recognized in 1974 by the Subgroup on "Analytical Methodologies for Soil, Sediment, and Water." A second meeting of that Subgroup and other experts was held in Ann Arbor, Michigan on May 8-9, 1975. The group agreed upon the material to be included in the Quality Control Handbook for Pilot Watershed Studies (QCH/PWS).

The First Issuance of the QCH/PWS was distributed to 124 participants in the PLUARG study on July 10, 1975. During the 1975 Field Season, the Handbook was a Working Document for Pilot Watershed Studies. Suggestions for improvements and corrections *were* requested from recipients.

The Handbook, as first developed, contained the following major Sections and protocols:

- 1. Introduction;      2. Parameter Lists;      3. Sample Collection;
- 4. Sample Handling;      5. Sample Preparation and Analysis;
- 6. Analysis Quality Control;      7. Data Handling and Processing;
- 8. Data Assessment;      9. References; and      10. Investigators.

For each of the major sections, sub topics were initiated as necessary. The first publication and subsequent changes and additions were of loose leaf binder type so that updating was made easy.

The First Revision of the QCH/PWS was issued in June 1976. The changes were largely changes in wording for clarification. The Second Revision of the QCH/PWS was made in March 1977. There were some additions and changes made in this Revision as follows:

Section 6. ANALYSIS QUALITY CONTROL -- was revised to show a re-assignment of responsibility. Mr. Robert E. White, Senior Scientist, IJC Great Lakes Regional Office, replaced Dr. Whitt on analytical quality control work.

Under Subsection 2.23 P. Mineralogy -- an additional reference was added:

Dell, C.I., 1973. A Quantitative Mineralogical Examination of the Clay-Size Fraction of Lake Superior Sediments. proc. 16th Conf. Great Lakes Research: pp. 413-420.

The new additions were:

- 7.4 REPORTING LOW LEVEL DATA
- 7.41 Codes to be used in Reporting Low Level Data
- 7.5 ESTIMATING TRIBUTARY LOADINGS
- 7.51 Ratio Estimator for Estimating Tributary Loadings
- 8.1 ASSESSMENT OF QUALITY CONTROL DATA

## QUALITY ASSURANCE PROGRAM

Having concluded the essential background summary toward the initiation of the Quality Assurance Program, the following will describe the activities that were undertaken during the development of the Handbook and later in direct response to the protocols set forth in Sections 6 and 8 of the document. In evaluation of these activities, both the successes and failures will be described.

Sections 6 and 8 of the Handbook provided protocols for the following:

- 6. Analysis Quality Control
  - 6.1 Blind Replicates from Field to Laboratories
  - 6.2 Reference and Natural Samples for Between-Laboratory Comparisons
    - 6.21 Reference Samples
    - 6.22 Round Robins
    - 6.23 Special Studies
  - 6.3 Documentation of Methodology
  - 6.4 In-Laboratory Quality Control
- 8. Data Assessment
  - 8.1 Data from Between-Laboratory Comparisons
  - 8.2 Annual Data

To meet these protocols several actions were initiated: interlaboratory analytical performance studies, blind replicate programs, and methods documentation.

### INTERLABORATORY ANALYTICAL PERFORMANCE STUDIES

To ensure that the analytical data generated by the various PLUARG Task C support laboratories were sufficiently precise and accurate as necessary for the studies at hand, and to demonstrate data compatibility between laboratories, 15 round-robin studies were conducted.

The studies were:

- 1 - Solid reference samples: some metals, nutrients and minerals, distributed May 1975
- 2 - Nutrients in Water, distributed August 1975
- 3 - Demand in Water, distributed August 1975
- 4 - Nutrients in Water, distributed October 1975

- 5 - Minerals in Water, distributed October 1975
- 6 - Trace Metals in Water, distributed October 1975
- 7 - Nutrients in Water, distributed December 1975
- 8 - Minerals in Water, distributed December 1975
- 9 - Trace Metals in Water, distributed December 1975
- 10 - Minerals in Water, distributed October 1976
- 11 - Nutrients in Water, distributed October 1976
- 12 - Pesticides in Sediments, distributed October 1976
- 13 - Pesticides in Water, distributed October 1976
- 14 - Metals in Sediments, distributed February 1977
- 15 - Mercury in Sediment, distributed February 1977

For each study specific instructions were supplied. The analyst after obtaining his results was to forward them to the Task C Basin Coordinator (later the Senior Scientist) for compilation and evaluation. The Coordinator in turn distributed the results on spread sheets with comments and an evaluation of test performances. If the laboratory supplied a description of the analytical methods used for the specific round-robin, this also was sent to each participant. The identity of a specific laboratory with respect to its results were not known by others participating. Only the Coordinator (later the Senior Scientist) had the identification key for all laboratories.

After the results were distributed, each analyst made comments on the performance of his laboratory and the overall round-robin results. These remarks, when appropriate, were combined and distributed along with additional comments and data revisions (if any) by the Coordinator or Senior Scientist.

If specific analytical problems were recognized of sufficient scope, the Coordinator or Senior Scientist personally consulted with the analyst and invited the project manager or contractor for whom the analyst was providing analytical services to discuss the matter. If the problem was not resolved it was taken up with the next higher authority.

#### 1. SOLID REFERENCE SAMPLES

At the second meeting of the Subgroup on "Analytical Methodologies for Soil, Sediment, and Water," a set of five (5) reference sediment samples provided by Mr. Frank C. Darcel of the Ontario Ministry of the Environment, were distributed for analysis. The sample types comprised of sand, lake deposit, Owen Sound, Kirkland Lake, and dried sewage sludge.

Each analyst was to return to his laboratory and immediately analyse the samples for iron, copper, zinc, manganese, nickel, mercury, chromium, vanadium, cobalt, lead, cadmium,

arsenic, nitrogen, and phosphorus.

The analysts that participated in this round-robin and their respective agencies or firms were:

- E. Beals, Bondar Clegg Limited, Ottawa, Limited
- C. Darcel, Ontario Ministry of the Environment, Rexdale, Ontario
- D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin
- R. Frank, Ontario Ministry of Agriculture and Food, Guelph, Ontario
- T. J. Logan, Ohio State University, Columbus, Ohio
- M. Reddy, New York State Department of Health, Albany, New York
- R. L. Thomas, Canada Centre for Inland Waters, Burlington, Ontario

As described earlier, each laboratory was assigned a number that was only known by the analyst and the River Basin Coordinator. From the results, the Coordinator in conjunction with the IJC Statistician prepared the following table to give each analyst a summary on how he compared with the others:

LAB NO.	SUM OF BORDERLINE CASES	SUM OF MORE OBVIOUS CASES OF INCOMPATIBILITY	TOTAL	NUMBER OF RESULTS PROVIDED	PERCENTAGE OF POSSIBLE DEVIANTS
1	3	0	3	69	4.3%
2	2	6	8	36	22.2%
3	8	5	13	70	18.6%
4	4	1	5	55	9.1%
5	1	0	1	50	2 %
6	0	0	0	45	0 %
7	3	0	3	55	5.5%

In addition to this summary presentation, specific results that looked out of line were highlighted. There were many obvious differences and the participants were invited to comment. From the comments received, inadequate sample digestion procedures and faulty atomic absorption tubes were identified as the principal causes for some poor metals results. In addition, because two laboratories widely differed they agreed to have a study between them to resolve the non-comparability of their metals data.

## 2. NUTRIENTS IN WATER

To establish not only whether laboratories could produce comparable data but also to evaluate laboratory accuracy, Mr. Harold Clements of the U.S. Environmental Protection Agency, Cincinnati, in August 1975, distributed a set of nutrient reference samples to 16 analysts. These reference samples were in ampuls and were to be added to water at the laboratory.

The following analysts participated in this round-robin:

- K. I. Aspila, Canada Centre for Inland Waters, Burlington, Ontario
- M. J. Capel, Freshwater Institute, Winnipeg, Manitoba
- W. Cook, Ontario Ministry of the Environment Laboratory, London, Ontario
- F. P. Dieken, Ontario Ministry of the Environment, Rexdale, Ontario
- M. D'Itri, Michigan State University, East Lansing, Michigan
- D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin
- A. Hinds, Ontario Ministry of the Environment, Rexdale, Ontario
- G. Kowalenko, Agriculture Canada, Ottawa, Ontario
- T. J. Logan, Ohio State University, Columbus, Ohio
- R. Osborne, University of Windsor, Windsor, Ontario
- N. K. Patni, Agriculture Canada, Ottawa, Ontario
- A. Richards, New York State Department of Health, Albany, New York
- J. B. Robinson, University of Guelph, Guelph, Ontario
- J. F. Sliwinski, Beak Consultants Limited, Rexdale, Ontario
- M. Thompson, University of Guelph, Guelph, Ontario
- R. J. Walker, Agriculture Canada, Harrow, Ontario

Instructions for diluting a 5 ml aliquot of each ampul to 1 litre were supplied. Although a sample expected range was known to the analysts, only the Coordinator knew of the true reference values for these diluted solutions. The values were in mg/litre:

Concentrate	NH <sub>3</sub> -N	NO <sub>3</sub> -N	PO <sub>4</sub> -P	Kjeldahl-N	Total P
1	0.44	0.20	0.021	--	--
2	1.47	1.11	0.393	-	--
3	--	--	--	0.35	0.142
4	--	--	--	5.80	0.713

Most laboratories performed triplicate analyses of the diluted ampul references. Overall the laboratories were able to obtain the reference values, though some laboratories which used specific ion probe had problems with their ammonia nitrogen determinations. One laboratory consistently reported values for phosphorus that were twice the target values.

### 3. DEMAND IN WATER

The purposes of this round-robin were identical to the previous one: to establish whether laboratories could get the same answer and to determine if their results were accurate. These samples were reference ampuls that were supplied by Mr. Harold Clements of the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

The participating analysts were:

- M. J. Capel, Freshwater Institute, Winnipeg, Manitoba
- W. Cook, Ontario Ministry of the Environment, London, Ontario
- F. Dieken, Ontario Ministry of the Environment, Rexdale, Ontario
- F. D'Itri, Michigan State University, East Lansing, Michigan
- D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin
- A. Hinds, Ontario Ministry of the Environment, Rexdale, Ontario
- T. J. Logan, Ohio State University, Columbus, Ohio
- A. Richards, New York State Department of Health, Albany, New York

The reference ampuls when aliquoted and diluted to the prescribed level produced the following target values in mg/litre:

Parameter	Sample 1	Sample 2
Total Organic Carbon	4.0	145
Chemical Oxygen Demand	10.3	370
Biochemical Oxygen Demand	3.1	186

These samples were expected to yield rather variable results for COD and BOD. The calculated theoretical COD target values assume complete oxidation of the samples to carbon dioxide, water, and ammonia. In actual practice, such theoretical values are very difficult to obtain. BOD target values were demands based on reported values in Standard Methods using river water as seed. The values obtained may or may not have been reproducible in a specific laboratory because of the natural differences in concentration and type of seed organisms from sample to sample.

As expected for BOD, laboratories had trouble in obtaining the target values and also in agreeing with each other. However, only in one case did a laboratory's value exceed a two-fold difference from the target value.

With one exception the TOC values were acceptably close to the reference values. The exception was a result of 28.6 mg/l TOC reported for sample 2, which was due to an error in calculation.

COD target values at the high level were in agreement between laboratories and fell only slightly below the target of 370 mg/l, yielding 355 mg/l on average. Laboratories had great difficulties with the lower COD reference sample, but experience dictates that this should be expected. Two laboratories reported 8 mg/l, being close to the target of 10.3 while the others reported 16 to 18 mg/l COD.

Additional communication between laboratories and the Coordinator stimulated corrective action; some additional tests resulted in more comparable data being reported.

#### 4. NUTRIENTS IN WATER

In October 1975, Messrs. P. Fellin and D. E. King of the Ontario Ministry of the Environment, Rexdale, Ontario, prepared and distributed a set of six samples. The samples were comprised of two composite river samples, two filtered river sample composites, a synthetic sample containing low concentrations (standards) of ammonium, phosphate, nitrite, and nitrate salts; and a second synthetic sample containing high concentrations of the above mentioned salts. Sample shipping problems prevented some analysts from participating.

Eight analysts, participated in this Nutrient round-robin; they were:

- F. Dieken, Ontario Ministry of the Environment, Rexdale, Ontario
- F. D'Itri, Michigan State University, East Lansing
- D. Glutek, Ontario Ministry of the Environment, Regional Laboratory, London, Ontario
- G. Kowalenko, Soil Research Institute, Agriculture Canada, Ottawa, Ontario
- M. Mazurski, Ontario Ministry of the Environment, Regional Laboratory,  
Thunder Bay, Ontario
- R. Osborne, University of Windsor, Windsor, Ontario
- J. F. Sliwinski, Beak Consultants, Mississauga, Ontario
- R. J. Walker, Agriculture Canada, Harrow, Ontario

Obvious differences were reported by some laboratories: one laboratory consistently reported higher Kjeldahl nitrogen results than others; another laboratory was low for ammonia. Results for phosphorus were generally quite good and overall, spike recoveries were obtained.

Some laboratory difficulties were identified and corrective action was taken. For example, one laboratory was able to identify their cadmium reducing column as the cause of low nitrogen results.

#### 5. MINERALS IN WATER

As for the previous study, Nutrients in Water, six round robin samples for minerals were prepared and distributed by Messrs. Fellin and King, Ontario Ministry of the Environment. The samples comprised of two composite river water samples, tap water diluted 10 to 1 with deionized water, tap water, tap water spiked with sodium, potassium, carbonate, sulfate, silicate, and chloride salts. The sixth sample was tap water spiked with calcium, magnesium, and chloride salts. The samples *were* distributed on October 1975, and the following analysts participated:

F. Dieken, Ontario Ministry of the Environment, Rexdale, Ontario  
 F. D'Itri, Michigan State University, East Lansing, Michigan  
 R. W. Gillham, University of Waterloo, Waterloo  
 D. Glutek, Ontario Ministry of the Environment, Regional Laboratory, London, Ontario  
 M. Mazurski, Ontario Ministry of the Environment, Regional Laboratory,  
 Thunder Bay, Ontario  
 R. Osborne, University of Windsor, Windsor, Ontario  
 J. F. Sliwinski, Beak Consultants, Mississauga, Ontario  
 R. J. Walker, Agriculture Canada, Harrow, Ontario

Obvious differences in results were identified by the Coordinator: one laboratory was lower in all cases for calcium, and all laboratories had difficulties in accurately recovering the potassium spike.

Five of the eight analysts commented on the results which were distributed to all analysts. Calculation errors were identified in several cases, and two laboratories were noted as having the greatest difficulty in agreeing with others. The evaluation of the round-robin is shown below:

LAB NO.	TOTAL NUMBER OF INCOMPATIBLE RESULTS	TOTAL RESULTS PROVIDED	PERCENTAGE
1	2	53	3.8 %
2	13	42	31 %
3	3	24	12.5 %
4	3	54	5.6 %
5	0	24	0 %
6	0	42	0 %
7	0	54	0 %
8	8	38	21 %

Further evaluation of the data and analysts' comments revealed that for many of the determinants a variety of different methods were applied. Those laboratories with the most variable results reviewed their methodology and took corrective action.

## 6. TRACE METALS IN WATER

Mr. James C. Daly, New York State Department of Health, prepared and distributed four water samples for round-robin analyses.

Two of the samples were simulated natural samples that were prepared by extracting trace metals from a sediment sample. The remaining two samples were a diluted reference standard, and a blank sample. The samples were distributed in October 1975.

Originally eight analysts were to participate in the round-robin but due to distribution problems, including broken sample bottles and lost samples, only four analysts were able to take part. The four participating analysts were:

F. D'Itri, Michigan State University, East Lansing, Michigan  
D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin  
M. Ihnat, Chemical & Biological Research Institute, Agriculture Canada, Ottawa  
T. J. Logan, Ohio State University, Columbus, Ohio

The samples were to be analyzed for chromium, copper, zinc, lead, iron, manganese, arsenic, mercury, cadmium, and selenium.

Initial analytical problems by one laboratory proved to be the calculation step (blank subtraction) and the results were corrected. Another laboratory had problems with their atomic absorption tube, which were subsequently corrected. The most difficult determinant was chromium; copper and cadmium results were also sporadic. The mercury results were in agreement.

## 7. NUTRIENTS IN WATER

As a result of the shipping problems experienced with the Nutrient samples distributed in October 1975, a second round-robin set was distributed in December. Mr. Don King, Ontario Ministry of the Environment, prepared and distributed the samples. Six samples were to be analyzed for total phosphorus, filtered total phosphorus, filtered (dissolved) reactive phosphorus, total nitrogen (or Kjeldahl nitrogen), ammonia, and nitrate plus nitrite nitrogen. The samples were prepared much the same as for the October study, i.e., natural river samples, and spiked river samples with ammonium, phosphate, nitrate, and nitrite salts.

Sixteen analysts (laboratories) participated; they were:

F. J. Philbert (Inorganic Lab.), Canada Centre for Inland Waters Burlington, Ontario  
F. J. Philbert (Ships Support Lab.), Canada Centre for Inland Waters,  
Burlington, Ontario  
B. Baker, Heidelberg College, Tiffin, Ohio  
E. Beals, Bondar Clegg Company, Ottawa, Ontario  
J. C. Daly, New York State Department of Health, Albany, New York  
F. Dieken, Ontario Ministry of the Environment, Rexdale, Ontario  
F. D'Itri, Michigan State University, East Lansing, Michigan  
D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin  
D. Glutek, Ontario Ministry of the Environment, Regional Laboratory, London, Ontario  
G. Kowalenko, Soil Research Institute, Agriculture Canada, Ottawa, Ont.  
T. J. Logan, The Ohio State University, Columbus, Ohio  
R. Osborne, University of Windsor, Windsor, Ontario  
J. Peck, Michigan Department of Natural Resources, Lansing, Michigan  
J. F. Sliwinski, Beak Consultants, Mississauga, Ontario  
L. E. Sommers, Purdue University, West Lafayette, Indiana  
R. J. Walker, Agriculture Canada, Harrow, Ontario

Reported results were quite scattered, especially for the nitrogen series. In addition to the obvious problems of sample handling (shipping and storage) several analysts felt that the

variable results obtained represented a non-homogeneity of the sample sets themselves. Blank problems were identified as the probable cause for sporadic nitrogen results coupled with preservation problems. The use of polyethylene containers was implicated in the failure to recover phosphate from these samples.

## 8. MINERALS IN WATER

As for the previously described Nutrient study, these round-robin samples were prepared and distributed by Mr. King of the Ontario Ministry of the Environment. Six samples, two natural river water, one near blank (2 litres tap + 18 litres deionized), one tap water, and two spiked with salts of sulfate, carbonate, chloride, calcium, and magnesium, were sent to fifteen participants. The analysts (laboratories) participating were:

- B. Baker, Heidelberg College, Tiffin, Ohio
- E. Beals, Bondar Clegg Company, Ottawa, Ontario
- W. Cook, Ontario Ministry of the Environment Laboratory, London, Ont.
- J. C. Daly, New York State Department of Health, Albany, New York
- F. Dieken, Ontario Ministry of the Environment, Rexdale, Ontario
- F. D'Itri, Michigan State University, East Lansing, Michigan
- D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin
- J. D. Gaynor, Agriculture Canada, Harrow, Ontario
- R. W. Gillham, University of Waterloo, Waterloo, Ontario
- T. J. Logan, The Ohio State University, Columbus, Ohio
- R. Osborne, University of Windsor, Windsor, Ontario
- J. Peck, Michigan Department of Natural Resources, Lansing, Michigan
- F. J. Philbert (Inorganic Lab.), Canada Centre for Inland Waters, Burlington, Ontario
- F. J. Philbert (Ships Support Lab.), Canada Centre for Inland Waters,  
Burlington, Ontario
- J. F. Sliwinski, Beak Consultants, Mississauga, Ontario

Results were distributed by the Coordinator. Some laboratories demonstrated high bias, especially on reactive silicates. As reported for some of the other studies, one analyst prepared the following table to yield a useful overview of laboratory performance.

LAB NO.	TOTAL NUMBER OF POSSIBLE DEVIANTS	# OF RESULTS REPORTED	% DEVIANTS
1	1	54	2
2a	3	54	2
3	24	42	57
4	1	54	2
5	1	54	2
6	-	30	-
7	-	42	-
8	1	54	2
9	24	48	50
10	1	24	4
11	2	42	5
12	5	30	17
13	3	24	13
14	-	12	-
15	7	48	15
2b	-	18	-

Responses from the analysts, especially from those laboratories that did not agree with others, indicated that corrective action had been taken to remove bias and to further check the instrumentation used.

#### 9. TRACE METALS IN WATER

Mr. James C. Daly, New York State Department of Health, prepared and distributed four samples. The samples were to be analyzed for chromium, copper, nickel, zinc, lead, iron, manganese, arsenic, cadmium, mercury, and selenium. The round robin samples were distributed in December 1975. Eight analysts (laboratories) participated; they were:

- J. C. Daly, New York State Department of Health, Albany, New York
- D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin
- F. J. Philbert (Inorganic Lab.), Canada Centre for Inland Waters, Burlington, Ontario
- F. J. Philbert (Ships Support Lab.), Canada Centre for Inland Waters,  
Burlington, Ontario
- M. Ihnat, Chemical & Biological Research Institute, Agriculture Canada, Ottawa, Ontario
- D. E. King, Ontario Ministry of the Environment, Rexdale, Ontario
- T. J. Logan, Ohio State University, Columbus, Ohio
- R. J. Walker, Agriculture Canada, Harrow, Ontario

Results from the collaborative test indicated that one method used by one laboratory gave consistently high values for lead. Most data appeared quite acceptable.

## 10. MINERALS IN WATER

Mr. P. Fellin, Ontario Ministry of the Environment, prepared six sets of check samples: a standard spiked water sample, a standard spiked sample different from the first, a third "normal" water sample, the third sample spiked with standards, the third sample spiked with more standards, and a 3 to 1 dilution of Toronto tap water with deionized water.

The samples were distributed at an analysts' meeting held at the Ontario Ministry of the Environment, Central Laboratory in Rexdale, Ontario, October 1976. Sixteen analysts (laboratories) participated in the interlaboratory comparison. The participants were:

J. Cherry, Department of Earth Science, University of Waterloo, Waterloo, Ontario  
F. P. Dieken, Ontario Ministry of the Environment, Central Laboratory, Rexdale, Ontario  
F. M. D'Itri, Michigan State University, East Lansing, Michigan  
D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin  
D. Glutek, Ontario Ministry of the Environment, Regional Laboratory, London, Ontario  
A. Hinds, Ontario Ministry of the Environment, Central Laboratory, Rexdale, Ontario  
J. Kramer, Heidelberg College, Tiffin, Ohio  
T. J. Logan, Ohio State University, Columbus, Ohio  
S. MacBeth, Ontario Ministry of the Environment,  
Kingston Regional Laboratory, Burlington, Ontario  
Mazurski, Ontario Ministry of the Environment, Laboratory, Thunder Bay, Ontario  
N.K. Patni, Agriculture Canada, Ottawa, Ontario  
F. J. Philbert (Inorganic Lab.), Canada Centre for Inland Waters, Burlington, Ontario  
F. J. Philbert (Ships Support Lab.), Canada Centre for Inland Waters,  
Burlington, Ontario  
A. Richards, New York State Department of Health, Albany, New York  
M. Sanderson, University of Windsor, Windsor, Ontario  
J. F. Sliwinski, Beak Consultants, Mississauga, Ontario

Each sample was analyzed for calcium, magnesium, sodium, potassium, alkalinity, chloride, sulfate, silicates, conductivity, and hardness.

Results were tabulated by laboratory, and each laboratory was ranked using the procedure described in Precision Measurement and Calibration, Statistical Concepts and Procedures, Special Publication 300, Volume 1, Ranking Laboratories by Round Robin Tests, W. J. Youden (165-9 -- 169-13) National Bureau of Standards. The procedure is designed to identify those laboratories that may be consistently reporting either low or high results.

Through the ranking procedure, the following problem results were identified by laboratory number:

DETERMINANT	RANKING RESULTS BY LABORATORY NO.	
	HIGH	LOW
Calcium	4	-
Magnesium	8	5?
Sodium	6,11,3?	-
Potassium	1?	2
Alkalinity	-	11
Chloride	3,15	11,12
Sulfate	8?	-
Silicates	13	
Conductivity	10?	2
Hardness	8	5

The ranking procedure only indicates when a laboratory is consistently reporting high or low values. To identify those laboratories with erratic performance, individual results were evaluated.

In general, recoveries on spiked samples were adequately obtained.

#### 11. NUTRIENTS IN WATER

These interlaboratory samples, as for the previous round robin 10 - Minerals, were prepared and distributed by Mr. P. Fellin, Ontario Ministry of the Environment. Sets containing six samples were prepared from deionized water spiked with standards, another deionized water spiked at a lower level, a composite of filtered natural river water, the river water composite spiked with standards, the river water composite spiked at a higher level than the previous, and a fresh sample of Humber River water. The samples were sent in bottles of polystyrene because of previous problems with polyethylene causing low phosphorus results.

The samples were analyzed for total phosphorus, filtered total phosphorus, filtered reactive phosphorus, total nitrogen, total Kjeldahl nitrogen, ammonia nitrogen, nitrate plus nitrite nitrogen, nitrate nitrogen, nitrite nitrogen, and organic nitrogen.

The samples were distributed in October 1976, to sixteen analysts. The participants were:

F. P. Dieken, Ontario Ministry of the Environment, Central Laboratory, Rexdale, Ontario  
 F. M. D'Itri, Michigan State University, East Lansing, Michigan  
 D. J. Dube, University of Wisconsin, State Laboratory of Hygiene, Madison, Wisconsin  
 D. Glutek, Ontario Ministry of the Environment, Regional Laboratory, London, Ontario  
 C. G. Kowalenko, Soil Research Laboratory, Ottawa, Ontario  
 J. Kramer, Heidelberg College, Tiffin, Ohio  
 C. K. Lee (for Robinson), Environmental Biology, University of Guelph, Ontario  
 T. J. Logan, Ohio State University, Columbus, Ohio  
 Mazurski, Ontario Ministry of the Environment, Laboratory, Thunder Bay, Ontario  
 N. K. Patni, Agriculture Canada, Ottawa  
 F. J. Philbert (Inorganic Lab.), Canada Centre for Inland Waters, Burlington, Ontario  
 F. J. Philbert (Ships Support Lab.), Canada Centre for Inland Waters,  
 Burlington, Ontario  
 A. Richards, New York State Department of Health, Albany, New York  
 M. Sanderson, University of Windsor, Windsor, Ontario  
 J. F. Sliwinski, Beak Consultants, Mississauga, Ontario  
 D. A. Tel, University of Guelph, Guelph, Ontario

Results received were ranked (as previously described) to yield the following table:

DETERMINANT	RANKING RESULTS BY LABORATORY NO.	
	HIGH	LOW
Total Phosphorus	5	-
Filtered Total. Phosphorus	6	12
Filtered Reactive PO <sub>4</sub>	-	-
Total Nitrogen	5	15
Total Kjeldahl Nitrogen	5, 2	15
Ammonia Nitrogen	2, 5?	9?
Nitrate + Nitrite Nitrogen	5	13
Nitrate Nitrogen	2	13
Nitrite Nitrogen	-	-
Organic Nitrogen	2, 5?	-

There was a surprisingly high spread among results. Some laboratories were quite erratic. Total nitrogen analyses were among the most scattered. The ranges for this constituent were as follows:

SAMPLE NO.	(RESULT SECOND FROM LOWEST)	RANGE mg/l (ALL RESULTS)	(RESULT SECOND FROM HIGHEST)
7	(1.45)	0.48--5.1	(3.03)
8	(0.50)	0.43--2.5	(2.2)
9	(0.98)	0.36--3.9	(1.44)
10	(1.25)	0.45--3.3	(2.04)
11	(1.95)	1.65--4.2	(3.05)
12	(0.75)	0.39--4.2	(1.18)

Discussions with the analysts revealed that two laboratories had changed personnel and that the new personnel were unfamiliar with the tests at the necessary level of method sensitivity. Furthermore, several of the laboratories were accustomed to water with much higher levels (wastewater) rather than tributary waters and therefore applied methods which lacked the necessary sensitivity for this round-robin.

## 12. PESTICIDES IN SEDIMENTS

Mr. Heinz E. Braun, Ontario Ministry of Agriculture and Food, prepared a sediment check sample from which he distributed sub-samples at an IJC analysts' meeting in Toronto, October 27-28, 1976. The sample was fortified with the following compounds in µg/g (ppm):

<u>Organochlorines</u>		<u>Organophosphates</u>	
p, p'- DDE	0.03	Diazinon	0.06
p, p' - TDE	0.05	Chlorpyriphos	0.08
Mirex	0.10	Leptophos	1.18
Oxy-chlordane	0.03		
α-chlordane	0.02		
γ-chlordane	0.02		
Dieldrin	0.008		
Endosulfan sulfate	0.032		
PCB	0.20		

### Phenoxyacid and Heterocyclic Herbicides

2,4-D	0.35	Atrazine	0.40
2,4,5-T	0.15	Simazine	0.60

Prior to fortifying the sample, a portion of the composite was tested for interferences and pesticides; it was found blank for the compounds of interest.

Messrs. M. Holdrinet, G. S. Sirons, and H. Braun of the Ontario Provincial Pesticide Residue Testing Laboratory, analyzed their prepared sample twice, on separate days, to see if agreement was obtainable. Their results follow:

Constituent (µg/g)	Spike Level	Nov.15	Nov. 22	Average Recovery %
Oxy-chlordane	0.03	0.019	0.022	71.7
γ-chlordane	0.02	0.016	0.018	85.0
α-chlordane	0.02	0.017	0.018	87.5
p,p'-DDE	0.03	0.024	0.026	83.3
p,p'-TDE	0.05	0.037	0.042	79.0
Mirex	0.10	0.050	0.055	52.5
PCB	0.20	0.19	0.19	95.0
Dieldrin	0.008	0.006	0.005	68.8
Endosulfan Sulfate	0.032	0.031	0.027	90.6
Diazinon	0.06	0.028	0.022	41.7
Chlorpyrifos	0.08	0.026	0.037	39.4
Leptophos	1.8	1.4	1.7	86.1
2,4-D	0.35	0.30	0.31	87.1
2,4,5-T	0.15	0.10	0.13	76.7
Atrazine	0.4	0.30	0.28	72.5
Simazine	0.6	0.51	0.50	84.2

A second laboratory reported results for the chlorinated hydrocarbons with duplicate analyses on days 1 and 14. Although this laboratory's findings differed from the other's, its replication (precision) was quite acceptable. This outcome is not unexpected for analyses of this difficulty. Results for the second laboratory follow:

	Day 1	Day 14	Average Recovery (%)
PCB	0.10	0.11	52.
	0.11	0.10	
p,p'-DDE	0.028	0.030	95.
	0.028	0.028	
Dieldrin	0.0017	0.006	44.1
	0.0034	0.003	
p,p'-TDE	0.026	0.028	55.
	0.028	0.028	
α-chlordane	0.013	0.013	70.
	0.018	0.012	
γ-chlordane	0.012	0.014	68.8
	0.017	0.012	
Mirex	0.055	0.055	51.3
	0.045	0.050	

It can be seen that the second laboratory failed to detect Endosulfan sulfate and oxy-chlordane. However, the samples were fully blind to them (totally unknown) and to discover 7 out of 9 constituents at the spiked levels was very credible, as many residue chemists would attest. The laboratory did not attempt to measure organophosphates, phenoxyacids or the heterocyclics that were spiked within the sample.

Other proposed participants (analysts) did not report their results.

### 13. PESTICIDES IN WATER

As with the Pesticides in Sediment study, this study too was designed by the Pesticide Analysis Subgroup of the PLUARG Watershed Study. The program was developed to provide information regarding (1) the quality of primary pesticide analytical standards in use by each of the participating laboratories, (2) the efficiency of pesticide extraction by the methodologies employed by each participating laboratory, and (3) the reproducibility within a laboratory and comparability between laboratories.

Three pesticide ampul sets were prepared by Mr. Braun (OMAF) and distributed to each participant at the Subgroup's meeting of October 27-28, 1976. The ampuls contained:

- |    |                           |    |                      |
|----|---------------------------|----|----------------------|
| 1. | p,p'-DDE 1.0 µg           | 2. | Aroclor 1254 5.0 µg  |
|    | p,p'-TDE 2.0 µg           | 3. | Diazinon 10 µg       |
|    | p,p'-DDT 2.0 µg           |    | Parathion 10 µg      |
|    | Endosulfan sulfate 5.0 µg |    | Ethion 10 µg         |
|    |                           |    | Azinphos-methyl 5 µg |

The solvents used for ampuls 1 and 2 were hexane, and for ampul 3, isooctane.

Instructions were provided on how to dilute the ampuls' contents so that a uniform protocol would be established and followed.

In addition to the chlorinated hydrocarbon and organophosphate standards in ampuls 1 through 3, another series of individual ampuls was distributed. This series comprised of separate ampuls containing separately 50 pg each of atrazine, simazine, MCPA, 2,4-D, and 2,4,5-T. As for the series 1 through 3, protocols for handling these ampuls were distributed.

In conjunction with the ampul samples, Dr. Frank D'Itre, Michigan State University, East Lansing, Michigan, had collected and distributed water samples taken from Mill Creek, Michigan. These samples were to compliment the standard ampuls and the ampul fortified water samples that were to be prepared in each laboratory.

For sundry reasons including shipping problems, few results were reported. One laboratory reported for the two water samples they received (hidden duplicates) the following results:

p,p'-DDE      0.001 and 0.0015 µg/l  
 PCB            0.03 and 0.03 µg/l

It is noteworthy that this laboratory was able to discern PCB and DDE uniformly at these low levels. The value of 0.001 µg/l is only 1 nanogram total (10 g) in a litre. Not many years ago 1 nanogram was just barely detectable by electron capture detection systems and such amounts still cannot be detected by alternative procedures such as microcoulometry or electrolytic conductivity.

Previous to this study and in preparation for it, the following four participants (labs) developed a water check sample program:

A. V. Rees            Ontario Ministry of the Environment, Rexdale, Ont.  
 J. R. W. Miles        Canada Agriculture, London, Ontario  
 R. C. J. Sampson    Canada Centre for Inland Waters, Burlington, Ont.  
 E. Braun              Ontario Ministry of Agriculture & Food, Guelph, Ont.

The purpose of this study was similar to that described for the 13 - Pesticides in Water. The following results were obtained:

Ampul (Standards)

COMPOUNDS	µg/ampul	LAB RESULTS µg/ampul		
		A	B	C
p,p'-DDT	2.00	2.06	1.96	1.84
p,p'-DDE	1.00	0.96	1.03	1.10
p,p'-DDD	2.00	1.92	1.90	2.09
Endosulf.Sulf.	5.00	5.0	4.90	N.A.
Aroclor 1254	5.0	5.0	4.60	5.0
Diazinon	10.0	9.9	9.70	8.4
Parathion	10.0	9.9	10.00	9.6
Ethion	10.0	9.7	9.80	9.0
Guthion	50.0	49.8	49.00	40.0
MCPA	50.0	50.0	N.A.*	N.A.
Dicamba	50.0	51.0	N.A.	N.A.
2,4-D	50.0	51.4	N.A.	N.A.
2,4,5-T	50.0	50.0	N.A.	N.A.
Atrazine	50.0	49.0	N.A.	N.A.
Simazine	50.0	45.4	N.A.	N.A.

\* Not Available

Fortified Water (Herbicides)

COMPOUNDS	Spike µg/l	FOUND µg/l			
		A	B	C	D
Atrazine	0.50	0.33	N.A.	N.A.	0.45
Simazine	0.50	0.54	N.A.	N.A.	0.95
Dicamba	1.0	0.37	N.A.	N.A.	0.95
MCPA	2.0	3.6	N.A.	N.A.	2.25
2,4-D	2.0	1.94	N.A.	N.A.	2.03
2,4,5-T	1.0	0.93	N.A.	N.A.	0.99

Fortified Water (Insecticides and Aroclor)

COMPOUNDS	Spike µg/l	RESULTS µg/l			
		A	B	C	D
p,p'-DDT	0.80	0.65	0.80	1.0	0.76
p,p'-DDE	0.40	0.27	0.36	0.41	0.33
p,p'-DDD	0.80	1.00	0.76	0.79	0.71
Endosulf.Sulf.	2.0	2.00	0.90	0.73	0.69
Aroclor 1254	2.0	1.65	2.05	N.A.	2.7
Diazinon	1.0	0.89	0.90	0.68	1.1
Parathion	2.0	1.60	1.95	1.7	2.1
Ethion	3.0	3.10	2.98	3.0	3.0
Guthion	20.	25.4	15.25	N.A.	26.
p,p'-DDT	0.06	0.04	0.07	0.086	0.04
p,p'-DDE	0.06	0.05	0.06	0.052	0.04
p,p'-DDD	0.10	0.12	0.10	0.102	0.08
Endosulf.Sulf.	0.18	0.20	0.10	0.054	0.11
Aroclor 1254	0.18	0.30	0.22	N.A.	0.24
Diazinon	0.08	0.08	0.08	0.046	0.09
Parathion	0.16	0.16	0.17	0.14	0.18
Ethion	0.12	0.12	0.13	0.13	0.13
Guthion	2.4	4.80	2.64	N.A.	3.1

By review of the data, it is quite clear that these laboratories are in good agreement considering the difficulty of pesticide analysis.

14. METALS IN SEDIMENT

Mr. K. I. Aspila of the Canada Centre for Inland Waters, prepared and distributed sediment samples to the following analysts (laboratories):

L. W. Costescu, Agriculture Canada, Ottawa, Ontario  
 F. Darcel, Ontario Ministry of the Environment, Rexdale, Ontario  
 J. A. C. Fortescue, Brock University, St. Catharines, Ontario  
 R. Frank, Ontario Ministry of Agriculture and Food, Guelph, Ontario  
 T. J. Logan, Ohio State University, Columbus, Ohio  
 F. J. Philbert, Canada Centre for Inland Waters, Burlington, Ontario  
 M. M. Reddy, State of New York, Dept. of Health, Albany, New York  
 C. Ross, U.S. EPA, Chicago, Illinois  
 R. L. Thomas, for Bondar-Clegg, Canada Centre for Inland Waters, Burlington, Ontario  
 T. K. Wu, Department of Natural Resources, Lansing, Michigan

With the six samples Mr. Aspila distributed, the analysts were requested that for each lot, if convenient, to determine these samples by (1) their method of choice, (2) Ontario Ministry of the Environment method (optional) and (3) 0.5N HCl non-residual metals procedure. Each participant was asked to measure lead, zinc, chromium, manganese, strontium, magnesium, tin, iron, copper, cadmium, aluminum, molybdenum, arsenic, selenium, nickel, cobalt, titanium, silicon in addition to total Kjeldahl nitrogen, calcium, lithium, apatite phosphorus, and total phosphorus.

The laboratories were assigned coded identification and their results were compared with each other by Mr. Aspila with the following findings:

PARAMETER OR CONSTITUENT	LAB CODE	SAMPLE NO.	COMMENTS
Lead	C	2	decimal point error
	B	(all)	errors?
	D	(all)	errors?
	C	2	(option 1 & 2, wrong order)
Zinc	B	(all)	errors (low)?
	C	1,3,4	high
Chromium	B	(all)	errors (low)?
	A & F	most	may be high or all other are low (volatile)?
Manganese	B	(all)	very low
	A	3	high (decimal)
	D & F	2	possibly high
Strontium		insufficient data	
Magnesium	J	4	(decimal error)?
Tin	C	(all)	possible high (insufficient data)

PARAMETER OR CONSTITUENT	LAB CODE	SAMPLE NO.	COMMENTS
Iron	F	(all)	tends to be low
	C	2	tends to be low
Copper	B	(all)	tends to be low
	G	6	high
	J	2	high
	D	4,5	low on most
Cadmium	B	(all)	low
	C	(all)	too high
Aluminum	All	(all)	variable due to methods (methods of choice)
Calcium	J	2,4,5	maybe low
Molybdenum	-	-	insufficient data
TKN	-	-	insufficient data
Arsenic	I	(all)	error (too high)?
Selenium	I	(all)	errors (too high)?
Nickel	B	(all)	low
	A	6	high
		I	high
Cobalt	C	(all) most	rather high
Titanium	-	-	insufficient data
Silicon	-	-	insufficient data
Lithium	-	-	insufficient data
Total P	-	-	OK
Apatite P	-	-	insufficient data
Mercury	-	-	OK

Mr. Aspila further noted that laboratory B was consistently low compared to others.

By the ranking procedure (previously described) laboratory B was reporting lowest of all laboratories for cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc. Subsequent discussion took place between the Senior Scientist, IJC, and the Principal Investigator to determine whether a cause for the low bias in results could be found, and further whether data from this laboratory could contribute to recommendations on watershed contribution to Great Lakes pollution.

## 15. MERCURY IN SEDIMENT

Mr. Aspila also distributed sediment samples for mercury analyses to the same participants as in the 14 - Metals in Sediment study. The method used was to be each analyst's choice. The seven laboratories that reported were in good agreement with each other even though the procedures used varied considerably in the digestion and reduction steps. The measurement technique used in all cases was cold vapor atomic absorption.

### Summary on Interlaboratory Studies

In summary, the round-robin sets were conducted to determine whether laboratories using their own methods for various chemical determinants could agree with one another, and if the results were also sufficiently accurate to allow the drawing of defensible research conclusions from the various watershed studies conducted under PLUARG Task C. For all laboratories but two, agreement and accuracy were adequate to support conclusions from combined studies. Appropriate steps were taken to ensure that data derived from the two laboratories did not affect the conclusions of the Task C Work Group.

### Additional Laboratory Checks

The Canadian support laboratories for PLUARG Task C determined in September of 1975 that they would develop an interlab duplicate program among their laboratories. Their program contained the following three elements:

- 1) Results of duplicate analysis of samples split at the laboratory for use in assessing in-laboratory precision.
- 2) Results of duplicate samples (separately Sampled, not Split) submitted 'blind' from the field to the laboratory for use in assessing the additional effect of field activities and sample type, or perishability, on precision.
- 3) Results of duplicate samples, where one would be analysed 'blind' by the support laboratory for the particular Task C study, and the other would be forwarded to the Central Laboratory of the Ontario Ministry of the Environment (OMOE) in Toronto, Ontario, for backup 'blind' analysis.

The intent of the program was to obtain a regular, continuing set of data, spread over the period of study covering those parameters of primary concern to the individual PLUARG Task C (Canadian) studies. Eight laboratories participated in element 3 to a greater or lesser extent over the period October 1975 to April 1977.

The eight laboratories that participated were:

Agriculture Canada, Harrow Research Station, Harrow, Ontario  
Drs. J. M. Fulton and R. Walker

University of Windsor, Windsor, Ontario  
Dr. M. Sanderson and Mr. R. Osborne

Agriculture Canada, Animal Research Institute, Ottawa, Ontario  
Dr. N. K. Patni

University of Guelph, Guelph, Ontario  
Dr. J. B. Robinson

Beak Consultants Limited, Rexdale, Ontario  
Drs. J. Sliwinski and P. Odam

University of Waterloo, Waterloo, Ontario  
Dr. R. Gillham

Brock University, St. Catharines, Ontario  
Dr. J. A. C. Fortescue and Mr. E. Veska

Ontario Ministry of the Environment, Toronto, Ontario  
Mr. D. Glutek and Dr. F. P. Dieken

The extent of the shared samples was as follows:

<u>Laboratory</u>	<u>No. of Samples</u>	<u>Time Period</u>
A	15	October 1975 - January 1976
B	27	November 1975 - June 1977
C	29	November 1975 - November 1976
D	74	November 1975 - May 1977
E	68	November 1975 - March 1977
F	60	May 1976 - May 1977
G	66	November 1976 - May 1977
H	16	September 1976 - December 1976

Mr. Don King, Ontario Ministry of the Environment, Rexdale, Ontario, assembled the results and has prepared an internal document on his assessment of the results. In his report, he summarized that the laboratories had no difficulty with the determinants sodium, potassium, alkalinity, chloride, conductivity, total phosphorus, silicates, total Kjeldahl nitrogen, and ammonia. He also concluded that for metals comparisons little useful data was obtained. Mr. King discussed some of the problems encountered in the measurement of calcium, magnesium, pH, suspended solids, turbidity, total iron, filtered total phosphorus, and filtered reactive phosphorus.

#### BLIND REPLICATES FROM THE FIELD TO THE LABORATORY

In addition to the within laboratory quality control measures, blind replicates were taken in the field and analyzed, allowing the project coordinator to determine whether the entire procedure was in control. Through this blind replicate procedure, assessment of

complete analytical variability could be made.

Section 6.1 of the Data Quality Handbook described the protocols to be used for the blind replicate program. The instructions state that replicate samples were to be taken in the field at the time and place of base line sampling schedule (not for special event sampling, unless specified by the project manager). These duplicates were to be taken at a rate of one site in replicate in any watershed or project with up to 25 sites and one more replicate within each increment of 25 sites over the first 25, e.g., 26 to 50 sites require two replicates, while 51 sites would require three, and so forth.

The replicate samples were to be separately sampled (not one sample divided and then sent to the laboratory). In addition, the duplicate samples were to be sampled as closely as possible at the same time and were to be submitted to the laboratory blind, with other field samples for routine analyses.

The Handbook instructions identified the project manager (leader, principal investigator) as responsible for designating the site and timing of replicate samples, and the ongoing evaluation of data derived from them. Further, this responsibility included giving prompt notification to the laboratory on their replicate results performances. The schedule and results of the replicate sampling were also to be reported to the River Basin Studies Coordinator (later the Senior Scientist).

All principal investigators, except one, that had research sampling included in their work which could lend itself to blind replicates did so. The kinds of projects that were unsuitable for duplicate sampling were typically non-homogeneity of sample matrix or when only one sample could be taken, for example, sediments and air-fallout.

The following people (organizations) provided data to the Coordinator as called for in the Handbook:

Mr. Dennis Onn, Hydrology and Monitoring Section, Water Resources Branch,  
Ontario Ministry of the Environment, Toronto, Ontario

Dr. D. Richard Coote, Engineering Research Service,  
Agriculture Canada, Ottawa, Ontario

Dr. Richard Frank, Ontario Pesticide Laboratory, Ontario Ministry of  
Agriculture and Food, University of Guelph, Guelph, Ontario

Dr. John A. Nicolson, Great Lakes Forest Research Centre,  
Environment Canada, Sault Ste. Marie, Ontario

Ms. Patricia Boulton, New York State Department of  
Environmental Conservation, Albany, New York

Dr. Roger Bannerman, Department of Natural Resources,  
State of Wisconsin, Madison, Wisconsin

Mr. Paul Odam, Beak Consultants Limited, Mississauga, Ontario

Dr. J. B. Robinson, Department of Environmental Biology,  
University of Guelph, Guelph, Ontario

Dr. Gregory J. Wall, Department of Land Resource Science,  
University of Guelph, Guelph, Ontario

Dr. Terry J. Logan, Agronomy Department, Ohio State University, Columbus, Ohio

Dr. N. K. Patni, Animal Research Institute, Agriculture Canada, Ottawa, Ontario

As one of its major purposes, the field duplicate program was designed to give flash results to the principal investigator so that if the sampling-sample handling-analysis procedure was out of control, immediate corrective response could be taken. How closely the principal investigators took advantage of this opportunity is not clear. However, analysis of several thousand results from the duplicate sample data did not suggest that any complete analytical system was out of control for an appreciable period of time.

In general, most of the replicate programs, as instituted, followed the protocols set forth in the Handbook. The respective principal investigators selected to examine the duplicate data in any manner of their choice, some simply "eyeballed" the information, looking for "outlier" duplicates; others developed standard deviations around paired data over set ranges, and still others treated their data in a mixture of these ways. Within all these cases some general statements can be made about the duplicate data.

Most duplicates matched quite well for almost all determinants. Of the several thousands of duplicates, overall only about five in one hundred would be considered of outlier quality. Five in one hundred may seem alarmingly high to a person not fully familiar with laboratory-field sample work, but this performance is very respectable.

The laboratories that processed many samples generally produced the best precision on the duplicate samples. There are some rational explanations for this, one being that a laboratory which is geared up to do the same thing in the same way over and over should do better than others. Another reason is that resources are present in a large laboratory to perform many internal checks as well as develop standard, rugged methods. Additionally, large laboratories frequently have automatic equipment that can repetitively perform a step in an analysis with greater precision than most analysts.

Particularly noteworthy is the fact that in terms of overall duplicate field sample-analyses, replicate samples matched each other much better than would have been heretofore suspected. The sampling crews must have exercised great care in sampling, and in sample storage and handling to have produced such uniform duplicate data.

The analyses within field duplicates that showed the most variability were suspended

solids, volatile solids, ammonia nitrogen, and nitrate and nitrite. The principal reason for duplicate difference in suspended and volatile solids was probably true constituent variability. Small differences in organic matter particulates (2 to 4 mg) could well account for the discrepancies. The variability in results for ammonia, nitrate, and nitrite nitrogen was probably due to the low levels of these constituents.

The duplicate program for pesticides and PCBs also demonstrated generally uniform pair results. Of the contaminants most found DDE, DDT, TDE, PCB, and atrazine, comparison at levels similar to 8 ng/l for DDE and 50 ng/l for PCB were excellent. In a few cases for phenoxyacid herbicides, one sample of a pair was negative while the other was in the 1.5 mg/l, range, which was quite likely due to "micro slugs."

## METHODS DOCUMENTATION

The Quality Control Handbook identified under Section 6.3 the protocols that were to be followed for documentation of methodology used. All project managers were directed to document their sample handling, preservation and storage, sample preparation, and final analysis technique. This information which was supplied to and filed by the IJC Great Lakes Regional Office was gathered as follows:

Questionnaires were sent to the project managers on analytical methodology and also on sampling and sample handling.

Within each round-robin (inter-comparison) study, a questionnaire or form was included, providing the analysts an opportunity to supply information on each method applied for each determinant.

The purposes for the documentation of sampling, sample handling, and analyses are obvious:

- (1) they assist in identifying possible causes of data inconsistency that are detected in the round robin comparison program so that the problems may be corrected;
- (2) they initiate a format that leads to discussion of the rationale for the use of differing methods and provide an opportunity for consensus on preferred procedures; and lastly,
- (3) they provide a permanent record of the procedures used by the participants during the various stages of the PLUARG Task C program.

Some 300 separate methods were submitted to the IJC Great Lakes Regional Office, ranging from sampling and storage of sample through individual analyses and analytical quality control. This documentation is available from the IJC Great Lakes Regional Office.

Also, during individual round-robin tests, methods used for specific tests have been submitted. As an example, one such summary is provided below:

Method Summary - Mercury in Sediment

LAB #	1	2	3	4	5	6	7
Sample Size							
Normal	0.3-3.0g	1.0g	0.5-1.0 g	0.5g	0.25-2.0g	1-2g	5. g
This Study	0.5g	1.0g	0.5g	0.5g	0.25-2.0g	1.0g	5..g
Digestion Procedure							
Bomb	No	No	No	No	No	Auto	
Open	✓	✓	✓	✓	✓		
Temp	100°	65°	95°	95°	60°		
Ratio & Mixture	HNO <sub>3</sub>	1	1	1	50	5	10
	HCl	3			3	2	
	H <sub>2</sub> SO <sub>4</sub>		4	2		10	conc. ✓ 5
	H <sub>2</sub> O		4				
Volume	4	20 ml.	5 ml.	20 ml.	17 ml.		10 ml.
KMnO <sub>4</sub>	✓	✓	✓	✓	✓		
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>			✓		✓		✓
H <sub>2</sub> O <sub>2</sub>							5 drops

LAB #	1	2	3	4	5	6	7
<b>Reduction</b>							
SnCl <sub>2</sub>	✓		✓			✓	
NH <sub>2</sub> -OH	✓			✓			✓
SnSO <sub>4</sub>		✓		✓	✓		✓
<b>Measurement</b>							
Manual	✓	✓	✓	✓	✓		
Automatic					✓	✓	
<b>Instrument</b>							
PE			✓				
Varian							
Coleman				✓			
Pharmacia	✓	✓			✓		
Technicon					✓	✓	✓
Spectro prod						✓	
Cold Vapor	✓	✓	✓		✓		✓

Most laboratories reported some form of intralaboratory control program, typically duplicate analyses of maybe 1 sample in 20, and some system of spikes and recovery checks for each determinant. Surprisingly, no laboratory reported using full system control charting to determine whether analyses were in control during a specified time period that allowed for immediate remedial action. However, the round-robin results together with the blind replicate results provide evidence that most laboratories performed adequately.