Norm Wade

Environment Canada | Environnement Canada

PROCEEDINGS

DATA COLLECTION QUALITY ASSURANCE WORKSHOP

Qualicum, October 27 - 28, 1993

HOSTED BY

Canada - British Columbia Water Quality Monitoring Agreement

Coordinating Committee

Prepared by Norma J. Wade

Environmental Conservation
Pacific & Yukon Region
Vancouver, B.C.

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DATA COLLECTION QUALITY ASSURANCE

October 26th

1900 - Dinner

October 27th

0830 - Introduction to the Workshop - Goals and Objectives - *Paul Whitfield* - Environment Canada

0850 - Integrating Quality Assurance into the Monitoring Process - *Malcolm Clark* - BCMELP

0920 - Calculating MDC's - Towards a Uniform Approach - *Dorothy Jeffery* - Zenon Environmental Laboratories

0950 - Controlling Sample Temperatures - *Tom Webber* - BCMELP

1020 COFFEE

1050 - Isomet - Contamination Free Sampling - *Bob McCrae* - Environment Canada - Ontario Region

1120 - pH Measurements - *Colin McKean* - BCMELP

1140 - pH Measurements - *Bruce Holmes* - BCMELP

1200 - LUNCH

1330 - Sampling through Ice Protocols - *Andrea Ryan* - Environment Canada

1400 - Quality Assurance for Electronically Acquired data *Norm Wade* - Environment Canada

1430 - Cyanide Workshop Update - *Malcolm Clark* - BCMELP

1500 - COFFEE

1515 - Proactive Quality Assurance for Contracted Analysis - *Robin Sampson* - National Laboratory for Environmental Testing - Burlington Ontario

1545 - Field Quality Assurance for Organic Contaminants - *Discussion*

1800 Dinner

DATA COLLECTION QUALITY ASSURANCE

October 28th

0830 - Data Validation and Approval Procedures - *Paul Whitfield* - Environment Canada

0900 - Standards - *Ian McLaurin* - Environment Canada - Ottawa

0930 - Work Group Sessions

- Blind Reference Samples
- Field Safety
- Field Filtration of Metals Samples
- Contract Labs

1130 - Plenary

1200 LUNCH

1345 - Mercury Issues - *Larry Pommen* - BCMELP

1415 - Suspended Sediments - Whole Bottle Analysis - *Norm Wade* - Environment Canada

1445 - The Changing Face of Monitoring - *J. Van Barneveld* - BCMELP

1515 - Closing Remarks

Introduction to the Workshop - Goals and Objectives

Paul Whitfield

On behalf of the Coordinating Committee of the Canada - BC Water Quality Monitoring Agreement, I would like to welcome you to this Data Collection Quality Assurance Workshop, and thank you for attending. We are gratified at the number of participants from other parts of Canada who have chosen to participate in the workshop. This workshop is focused on quality assurance around water quality sampling, but the principles can be applied to other types of data collection as well.

We intend the workshop to be an open forum on all aspects of quality assurance and I would like to encourage each of you to contribute to the dialogue through comments or questions.

Quality assurance must be proactive. We have no proven mechanisms for correcting bad or suspect data. We have an ongoing need for our data to be credible. To achieve this significant efforts must be put into collecting good well documented data. At a recent meeting I attended one of the authors speaking on quality assurance put up the following equation:

$$O_t = R_t + E_1 + E_2 + E_3 + E_4 \ldots + E_n$$

The observations (O) we make at over time (t) are really the real values (R) combined with a series of errors (E). These errors include sampling, preservation, handling, storage, analysis etc. While this may be daunting view, it is a good picture of the reality of data collection.

The presentations and discussions of the papers which follow should provide some insight into the problems and solutions involved in quality assurance. More than any one individual action, we must work together towards the common goal of obtaining "good data."

INTEGRATING QUALITY ASSURANCE INTO THE MONITORING PROCESS

Malcolm J. R. Clark

British Columbia

Ministry of Environment, Lands, and Parks

WATER RESOURCES BULLETIN
VOL. 29, NO. 1 AMERICAN WATER RESOURCES ASSOCIATION FEBRUARY 1993

A PRACTICAL MODEL INTEGRATING QUALITY ASSURANCE INTO ENVIRONMENTAL MONITORING[1]

Malcolm J. R. Clark and Paul H. Whitfield[2]

ABSTRACT: A model of comprehensive environmental monitoring process with integral quality assurance is presented. This model views the monitoring process as iterative cycles of a series of elements: design, plan, protocols, preparation, field liaison, sample collection, sample handling, laboratory analysis, data transmission, data validation, data approval, data provision, statistical analysis, and reporting. Quality assurance is linked to each element, not just to laboratory analysis. The program of quality assurance ensures that environmental monitoring data are compatible with the project goals, are comparable between various sampling agencies, and maintain a high degree of scientific credibility. The key characteristics of the overall quality assurance process are detailed documentation, timely resolution of problems, regular reporting, and routine independent audits.
(KEY TERMS: environmental studies; modeling/statistics; monitoring; quality assurance; study design; water quality.)

INTRODUCTION

Quality assurance applies to each step of the environmental monitoring process, and not only to those quality control procedures carried out in laboratories. This paper outlines a model of the complete data collection and analysis process in terms of integral quality assurance. The model is based on the use of best available practices, detailed protocols and appropriate documentation of methods, and deviations from procedures. Together these provide a level of assurance which allows the data to be of scientific value in the future or to other researchers. In addition, each step in the process of environmental monitoring has some specific requirements that apply to at least that step. This entire process sometimes is referred to as "Quality Assurance" or "QA," and sometimes as "Quality Assurance/Quality Control" or "QA/QC." In the latter case, QC refers to those aspects which are fully under an investigator's personal control (such as instrument calibration or comparison to reference materials of known value), and QA refers to those aspects which are not under the investigator's routine control (such as analysis of reference materials of unknown value for evaluation by an independent party). Not surprisingly, these two different definitions for "QA" result in semantic confusion. For this paper the authors use the first, more comprehensive, definition for the synonyms "quality assurance" and "QA."

Under ideal circumstances, scientific data are collected from carefully controlled experimental conditions which may be repeated should any question of data validity arise. However, environmental monitoring data are collected under conditions which are imprecisely controlled and difficult or impossible to repeat. In view of these problems, researchers must ensure that their environmental data are scientifically credible by documenting their adherence to proven scientific practices. For uncontrolled conditions, these practices include detailed documentation of procedures, ongoing evaluations of precision and accuracy, and regular independent audits. Together these documents provide a complete chronological record to support the validity of the data.

This paper describes a data collection and analysis model which provides the framework for integrating quality assurance into all elements of environmental monitoring. The paper also describes those quality assurance activities that are common to all steps in any environmental monitoring process, and provides

[1]Paper No. 92112 of the *Water Resources Bulletin*. **Discussions are open until October 1, 1993.**
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example applications from a water quality perspective.

THE ENVIRONMENTAL MONITORING PROCESS

The model of the environmental monitoring process is presented schematically in Figure 1. The model views the monitoring process as an ordered series of linked elements covering all activities in the data gathering process. Each element in the cycle is subject to changes and enhancements over time, reflecting changes in knowledge or improvements in methods and instrumentation. Therefore, each element must have defined quality assurance activities to monitor these changes.

There are several advantages to this type of model. First, it serves as a visual tool scientists can use when organizing the budgets and manpower resources for a project so as to ensure all aspects of a project receive an appropriate share. Second, the model emphasizes that data are no better than the weakest link, and therefore all elements must provide QA. Third, the model reminds us that, even if each element itself has appropriate QA, problems may occur in the links between elements. Therefore, we must take steps to ensure the links between elements are closely examined as well as the elements themselves. Fourth, the model shows that, if one waits for information to follow the complete cycle, problems may not be identified and resolved on a timely basis. Therefore, a negative feedback mechanism is an essential part of the process.

Environmental monitoring requires a large investment of resources. Appropriate quality assurance

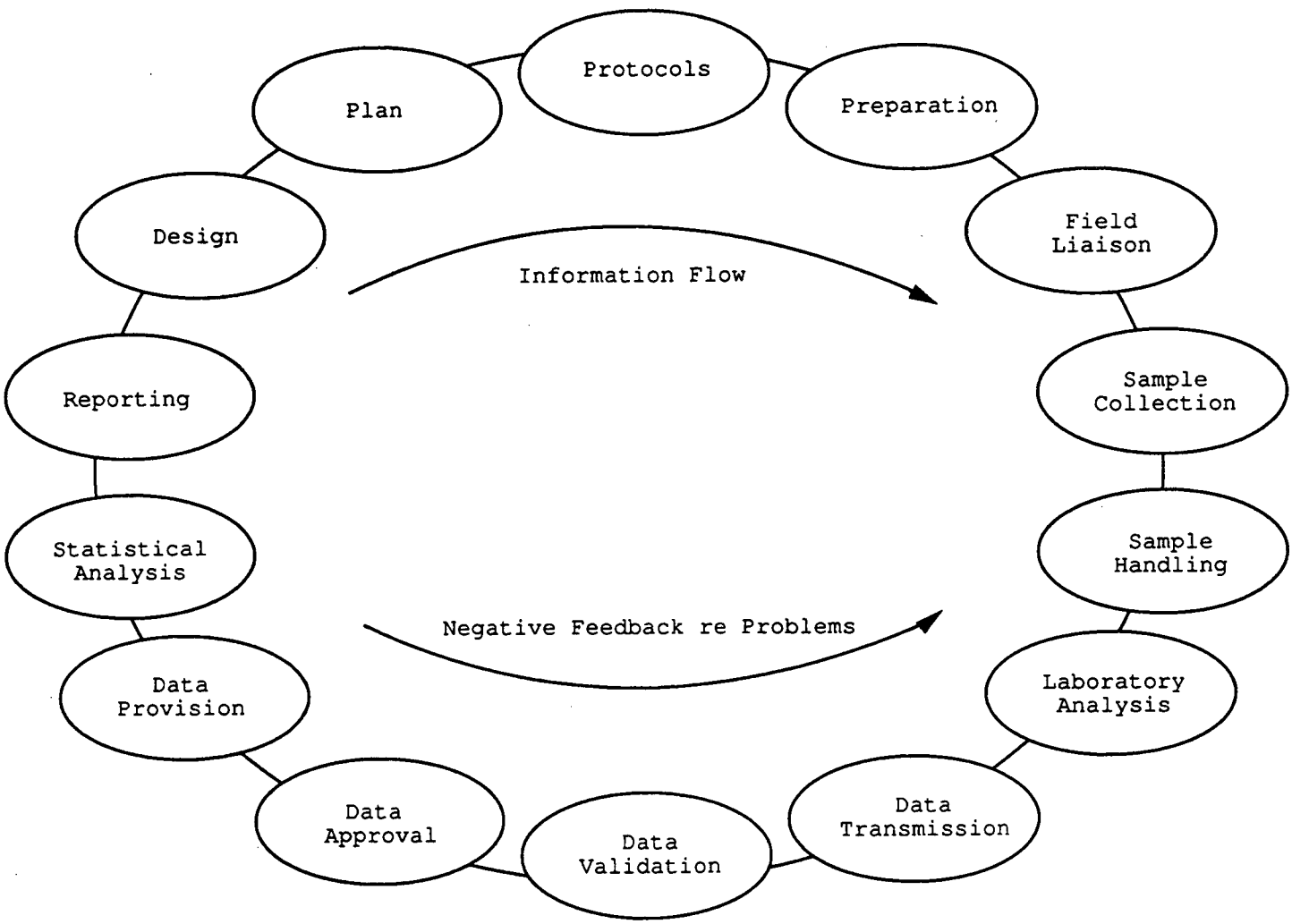

Figure 1. Fourteen Element Iterative Cycle Model of the Environmental Monitoring Process.

provides a mechanism which protects that investment. Proactive steps are taken which seek to eliminate flaws and errors before they compromise the quality of the data that are being collected. Mohnen (1992) points out that QA programs have benefits which include less replication of effort since poor quality studies often must be redone. Mohnen (1992) emphasizes that the greatest benefit to be derived from a QA program is confidence in the results by staff, clients, and peers. Conversely, we have noted a "QA Paradox" whereby unexamined programs may be viewed by some parties as superior to examined programs, since the unexamined programs have no known problems. This "QA paradox" must be avoided through education of parties unfamiliar with the QA process, and through emphasis within QA reports upon successes rather than upon problems.

ELEMENTS OF THE ENVIRONMENTAL MONITORING MODEL

Element 1: Design

Environmental monitoring programs must be based upon effective strategies to meet specifically defined goals. Many papers point out this need to link monitoring activities to environmental management goals (Lettenmaier, 1978; Ward, 1979; Schilperoort and Groot, 1983; Ward *et al.*, 1986; Whitfield, 1988). However, a somewhat cavalier attitude still persists for many environmental monitoring programs. It must be emphasized that data collected for one specific purpose may not be appropriate for some entirely different purpose. Also, data collected without any formal purpose may be useful for very few specific future purposes. It is a fallacy to suppose that poor data are better than no data.

The logical starting point for any study is the design step. All monitoring programs must have a formal design before any work is initiated. The most important parts of any design are a clear delineation of the study area, plus clear tabulation of the study goals. These goals provide direction in the planning of the data collection process. The five goals most commonly identified for environmental monitoring include (a) assessment of trends in variables of concern, (b) compliance with objectives or standards, (c) estimation of mass transport, (d) assessment of environmental impact, and (e) general surveillance to determine typical levels of environmental quality over a broad spatial area (Whitfield, 1988).

Quality assurance for the design process includes the delineation of specific goals and geographic area while ensuring that the data collection strategies are appropriate to these goals. Millard (1987) has pointed out that serious program flaws can occur if only superficial consideration is made of statistical concerns at the design stage. Study area, design goals, and sampling strategies should be optimized as new information comes available. The cyclic model ensures that these topics are reviewed and optimized on a regular repeated basis at least once per study cycle.

Element 2: Plan

The Plan is a working document which can be distributed to all the study participants so each party knows in some detail precisely what is expected of every participant. The Plan must include schedules and budgets for every job to be done within all elements of the monitoring cycle for not less than one complete project cycle. The Plan structures the process and defines the tasks and steps required to attain each goal. In a sense, if the Design is considered an outline sketch of a project, then the Plan is the corresponding detailed blueprint. Budgets, schedules, manpower resources, manpower training requirements, safety programs, and vehicle and equipment requirements all must be detailed within the Plan.

The QA aspects of the Plan element need to focus on ensuring timely identification of variances from the schedules or budgets. Additionally the QA aspects of the Plan must ensure that good communications are taking place between those participants undertaking interlinked activities.

In preparing the Plan plus the related QA program, it is useful to test the draft Plan with either a Pilot project or with a mock project using surrogate data. Such studies will optimize cost-benefit ratios, and will assist towards early identification of conflicts between study participants with regard to objectives, schedules, or methods. Analysis of existing data sets can be usefully employed to ensure adequate sampling to determine genuine effects or trends, or conversely to weed out inappropriate sampling programs which are unlikely to determine any effects for the resources available.

Element 3: Protocols

The Protocols, sometimes called Standard Operating Procedures (SOPs), are formal written procedures of all methods to be followed during the course of the project. Included in the Protocols are details as to how actions are performed and what

records are to be kept. Examples include sample collection and preservation in the field, laboratory procedures, data recording, and computer processing.

The Protocols must require reporting of quality assurance results on a regular and timely basis, and also must specify acceptance criteria for specific QA/QC programs. Additionally, the Protocols must ensure that all data, including handwritten results and the Protocols themselves, are protected against loss. Thus, one or more duplicate copies of information must be kept in separate and secure locations. The Protocols must also include provision for reporting all exceptions-to-the-rule or nonconforming events, since our experience suggests it is nearly impossible to avoid exceptions under real world conditions. It is also our experience that exceptions and problems need to be communicated rapidly between study participants to avoid misunderstandings or repeated use of flawed procedures. The Protocols need not duplicate already published Methodology Reports, such as laboratories often publish. However, where multiple methodologies exist, where existing methods have been modified, or where new methods have been implemented, it is important that the exact details of the methods be documented.

The Protocols must be completed before sampling commences, and must be kept up-to-date on an ongoing basis. Failure to do this may result in problems serious enough to invalidate the main data sets. Our experience with interagency studies has shown that those studies were most successful which had a formal signoff procedure to authorize the Protocols and changes to the Protocols. Wherever possible, international protocols must be used so as to make the data compatible with similar information collected in other countries.

Within any particular environmental monitoring program, collective understanding of the procedures being used greatly enhances the quality of the data being gathered, and all members of the study team should be encouraged to contribute to the Protocols. Busy staff members will do a better job if they understand the practical purpose of some job. Adequate documentation of all methodology enhances the potential for future use of the collected information, possibly decades or centuries into the future. With this long term repeat use of the study information in mind, all Protocols must be published or placed in archive with national libraries, public archives, or with international agencies.

The QA aspects for the Protocols element must ensure both that the Protocols are up-to-date, safely archived, and correspond to genuine practices. Our experiences indicate two common problems which require extra effort to avoid. First, an agency may honesty believe a particular methodology is being followed, but had, in fact, lost track that these procedures had been changed. Second, agencies may report no methodology change for some variable over a number of years, yet the data themselves clearly reflect stepwise increments in method sensitivity. Our experience suggests that latter problem usually results from a failure in communication, either between the laboratory chemists and the data processing staff or between the laboratory and its clients.

Element 4: Preparation

The Preparation element includes those activities which take place prior to sampling and away from the sampling locations. Activities include purchase of materials and equipment, preparation of sampling bottles and of reagent chemicals, maintenance and calibration of equipment, and also shipping of sampling kits and equipment to remote areas.

Quality assurance for preparation must ensure that maintenance logs and calibration records are maintained for every scientific instrument. Also, materials such as sample bottles and reagents must be routinely checked to ensure they meet specifications. Our experience suggests three common problems: (1) overreliance on manufacturers' specifications, (2) presampling sources of contamination, and (3) late or incomplete shipments of materials and supplies to field crews. Specifications supplied with instruments are often found to be optimistic. With regard to the contamination problem, we have found that reuse of either sample bottles or preservation vials for trace elements both are likely causes of contamination. Also, late or incomplete shipments can be very frustrating to field staff and can cause serious program interruptions, often with significant interruptions to the data records. A proactive approach, which prevents problems rather than resolving them, is the optimum approach. QA programs must attempt to identify such problems as early as possible during the course of a study.

Element 5: Field Liaison

Field liaison covers communication between headquarters and field staff which must be two-way as partners rather than master-servant. Field staff must be provided with the necessary skills and equipment to do the job adequately and safely. Both headquarters and field staff must be thoroughly educated with regard to safety concerns and also as to proper use of vehicles and equipment. Headquarters must be advised when exceptions to regular routines occur

and also when problems, such as late delivery of equipment and supplies, happen. Where authority is delegated to field staff, the accompanying responsibility and accountability must be delineated.

Poor communications can result in even trivial problems being blown out of proportion, while serious problems may be only slowly recognized and resolved. Also staff training must be ongoing, and must be repeated frequently where changes in personnel are frequent. From our experience, we have found that field liaison goes far more smoothly when semiformal paper records of all communications between headquarters and field staff are maintained, and also when headquarters and field staff undertake some joint operations.

Quality assurance checks for field liaison verify that both communication records and training records are maintained complete and up to date. The quality assurance procedures additionally must attempt to identify and minimize or resolve misunderstandings between headquarters and field teams. This type of problem often can best be identified through investigation of deviations from schedules in the Plan or from methods defined in the Protocols.

Element 6: Sample Collection

The Sample Collection element encompasses those activities which take place immediately before and during actual collection of samples from the environment. These activities include site selection, sample collection plus on-site sample handling, in-situ measurements, photography and other means of observation, and the keeping of all related records. Also included are on-site care and calibration of field equipment. (Off-site care and calibration of equipment is part of Preparation.) As noted by Brown *et al.* (1991), detailed notes taken during the sampling process often are invaluable during data interpretation steps.

The associated quality assurance must ensure that all relevant details are recorded, especially deviations from defined procedures. The QA must also ensure that all Protocols were followed, including those related to the QA part of the Plan. Five major QA concerns are: (1) completeness of sample collection, (2) representativeness of samples, (3) unique identification of each sample, (4) documentation of the characteristics of each sample, and (5) recognition of external contamination. The authors have found that early warning of missing samples can often be noted in program costs (i.e., unexpected low costs), which accounting staff usually keep fairly up to date. With regard to the representativeness of samples, gradients (e.g., mixing zone at the confluence of two rivers) should be recognized through in-situ measurements and, where possible, avoided. If gradients must be sampled, then the Protocols must specify some formal strategy of replicate samples or composited samples to be followed. Samples are best identified by being immediately labeled with a unique number. All samples must be thoroughly described as to precise sampling location, date and time, collector, collection equipment, site conditions, sample details, and unusual features or events. Contamination is best identified through use of a formal program of blanks. A field blanks program must be maintained on a regular basis, with contingency provisions for a major effort to resolve any contamination problem once identified.

Element 7: Sample Handling

The Sample Handling element includes all activities which take place between collection of samples and receipt of those samples by some scientific institution for cataloging or for detailed scientific analysis. These activities typically include various sample manipulations, including preliminary measurements, sample preservation and packaging prior to transportation, plus the transportation step itself.

The quality assurance for Sample Handling assures sample integrity and identity. Positively no foreign object must be placed into any sample bottle, with the sole exception of preservation reagent. This includes stirring rods, thermometers, dissolved oxygen probes, and conductivity probes. If measurements must be made on site from a portion of the sample, then, ideally, this should be an extra portion which can be discarded, or at least kept separate from the remaining sample portions. For water samples, such field measures should be made in-situ or else from a unique bottle used for no other purpose. If samples must be manipulated (for example, water samples might have to be filtered), then the Protocols must include detailed methods for both the manipulation and for related QA/QC sampling (e.g., filtration of a field blank). The Protocols must also detail requirements as to sample identification, chain of custody (if required), and preservation.

Some samples may be unstable under certain conditions. Therefore, the QA Protocols must specify acceptable conditions, such as allowable temperature ranges and appropriate preservation methods. It is common for water samples to be cooled with ice between time of sample collection and receipt by a laboratory. From the authors' experience, it should be appreciated that large volume water samples in a cooler with a small mass of ice may arrive at a laboratory too warm in summer or frozen solid in winter. Therefore, the samples must be inspected on receipt

at the laboratory, and the status recorded. Also, even with preservation, some types of samples will slowly deteriorate over time. Therefore, QA Protocols must specify maximum acceptable delays between time of sample collection and time of analysis for specific variables. The goal of Sample Handling QA programs is to guarantee that the QA Protocols were rigorously enforced, and any exceptions unambiguously identified.

Element 8: Laboratory Analyses

Most environmental studies require sample analysis by one or more laboratories, whether physical measurements, bacteriological analyses, bioassay testing, chemical analyses, or taxonomic identifications. Most laboratories will have their own in-house QA/QC programs. However, these in-house programs will not suffice to replace comprehensive Project QA. The Project QA must ensure that laboratories report both data and their associated in-house QA results on a timely basis. It is important that a process be in place to ensure methodology changes at a laboratory are immediately recorded in data management systems. The authors have found that, where laboratories report data in machine-readable form, they sometimes are tempted to ignore important method changes so as not to interfere with the smooth flow of the data to the client. This practice is best discouraged by requiring signature authorization for method changes.

Project QA results should be published in detail and not kept confidential. The Project QA program must include submission of reference samples, blanks, and spiked samples to the analyzing laboratories, some portion of which must be on a blind basis (i.e., the laboratory staff must be unable to distinguish the QA samples from genuine environmental samples). If true sample blindness is not possible, then this should be recognized and steps taken towards establishing sample blindness. For example, if sediment samples are wet but associated QA samples are freeze-dried, then it makes no sense to pretend the samples are blind. Rather, true blindness must be re-established, possibly by freeze-drying some genuine samples.

The Project QA must also ensure that laboratories themselves maintain comprehensive in-house QA/QC programs. Laboratories need not publish detailed results from these in-house programs, as they may include confidential and proprietary information. However, the results must be published in summary on a regular and timely basis, and full details must be maintained for not less than five years in case questions of possible sample contamination or similar problems arise during the data interpretation steps. After five years, these results should be placed into a permanent archive, though confidentiality may be maintained for several decades. If practical, some statement of QA/QC results should appear directly upon the laboratory reports of results. Our experience suggests that laboratories primarily focus upon providing the best results on a sample-by-sample basis, while looking forward to improving methods for future samples, but with little interest concerning the QA/QC of samples they analyzed five or ten years ago. Laboratories must be encouraged to realize the long-term existence of these data, the need to document chronological details of method changes, and the need to preserve methodology details and QA/QC information into permanent archives. For samples undergoing taxonomic identification, laboratories must publish details as to identification keys used, level of identification, staff expertise, plus verification steps including creation of reference collections and photographic catalogs.

The Project QA program must also include occasional inspection of the laboratory facilities. King (1982) notes that the following areas need to be addressed to establish laboratory credibility: condition of the laboratory facility, condition of the analytical equipment, quality of the reagents, availability of documented analytical methodologies, existence of documented internal QA protocols, proficiency and experience of the analysts, and the reliability of calibration materials, in-house controls, and external reference materials. To this list the authors suggest adding the requirement for a full-time quality assurance officer. While QA/QC needs to be every scientists' responsibility, nonetheless, our experience leads us to believe that the best programs do have a single person clearly identified as having QA as his or her major responsibility. The QA Officer must be separate from laboratory management, since the role of minimizing budget costs often may be in direct conflict with the role of maximizing data quality.

Element 9: Data Transmission

Laboratories usually convey results of chemical or other analyses to their clients, either as printed reports from a computer data base or as file transfer from computer to computer. Even when data are transmitted via printed records, at least some portion of the results may be manually re-entered onto another computer system. Thus, at least one computer and sometimes two or more computers may be involved in validating data and manipulating results. Agencies either transmitting or receiving the results may modify the data, possibly by error. Errors may occur during electronic data transmission, especially in

situations where data move through a number of different computer systems.

The Data Transmission element covers all those operations where data are likely to be changed as part of the laboratory reporting process or the arranging for results to be accepted into another agency's record holdings. Three common types of operations which take place are calculations of some variable result based on two or more other variables, some type of validation procedures, and censoring of data. An example of a calculation would be calculation of nonfilterable residue as the difference between total residue and filterable residue. An example of a validation procedure would be a check to ascertain whether the dissolved form of a metal exceeds the total form by an amount in excess of some defined criterion. Various types of data censoring commonly occur. These include merging of results from analyses of several aliquots into one value, rounding off to significant digits, deletion of all results below some detection limit cutoff, and nonreporting of results which fail a laboratory's in-house validation. The authors would prefer that laboratories abandon censoring and suggest as an alternative the presentation of data as measurement-uncertainty or measurement-reliability data pairs. Porter and Ward (1991) note that censoring data increases bias and that censored data require more complex and less familiar statistical procedures than analogous methods for uncensored data.

A project's QA Protocols must ensure that a permanent and complete record is established as to what algorithms and code were used in flagging, checking, calculating, validating, censoring, or otherwise processing the data. These records should all be placed into some permanent archive. Of particular concern is that samples be correctly identified and that any post-receipt modifications to the data whatsoever be fully documented. Additionally, every laboratory plus every analytical method must be uniquely identified on the data records. If a method's sensitivity changes due to methodology changes or due to instrumentation changes, then the transmitted sample method code must be of sufficient detail that there positively is no ambiguity as to which sensitivity relates to which subdata set. Since different scientists often have very different views of the validity of various calculations and data censoring activities, it is important that the exact procedures be fully documented. The authors strongly concur with Porter's *et al.* (1988) argument that censoring of analytical results by reporting laboratories should be discouraged and that measurement precision must always be reported.

The four most important jobs the QA Protocols must ensure with regard to Data Transmission are that: (1) every sample is correctly identified, (2) a clear audit trail exists for every formal change or correction made to the original data, (3) informal or accidental changes to any results are impossible, and (4) all data files are fully backed up at some secure location so that data loss in case of disaster will be minimal.

Element 10: Data Validation

During Data Validation, all data values are examined and prepared for Approval and Publication. The Data Validation element includes all those validation checks made after receipt of results from the analyzing agency. This element covers checks of the data themselves, whereas the previous element covered checks of the systems holding and manipulating the data. Data Validation checks typically include statistical analysis of replicate and spiked sample data, of blanks and of standard reference materials data, and also of the historical data records. Where more than one agency is sampling a study area, then having several sites where the agencies sample simultaneously will yield data very useful towards ensuring the agencies are collecting comparable data. Though some initial steps of data validation can be done by computer, we recommend that a knowledgeable scientist must confirm any computer-generated validation results. We also recommend that questionable data be flagged or moved to a secondary file, rather than being destroyed. Even suspect data often contain some informational content.

The QA Protocols regarding Data Validation must include details as to what methods and checks are to be utilized to ensure the data on record are valid. Where multiple laboratories are involved in analyzing samples, then statistical methods of interlaboratory comparisons must be considered during data evaluation. There is considerable recent literature on this topic, for example Aspila (1989), Mesley *et al.* (1991), and Gaskin (1991). The QA Protocols should also ensure that, at the conclusion of the study, all machine readable data are deposited in an archive with an institution specializing in holding archival computer records.

We recommend that all data be fully validated so as to maximize usefulness of the information. Some agencies, however, prefer to give a judgmental ranking as to the quality of the data. For example, PTI Environmental Services (1991) recommends four levels of Data Validation: Level 1 Validation pertains to all sample data and all laboratory QC data, Level 2 Validation covers either critical elements or representative subsamples, Level 3 Validation includes a

cursory review of summary results only, and Level 4 Validation does nothing beyond regular internal laboratory QC studies.

Element 11: Data Approval

The Data Approval element gives formal acceptance of the values obtained as being within the acceptance criteria established. Approved data may be released or published as having been officially "Validated." We have separated the concepts of Data Validation and Data Approval, since the focus of the former is on finding and dealing with errors, whereas the focus of the latter is upon the release of the validated results. Data released for publication, without having gone through the entire Data Validation and Data Approval process, must be clearly identified as "Preliminary" or "Not Validated." The Approval process must always be a formal process where the reviewers formally, through signature, take responsibility for the data being scientific level quality.

Quality Assurance Protocols for Data Approval ensure that there is a clear distinction made between validated and nonvalidated data. If different levels of data validation have been used through a study, then the QA Protocols must ensure that there is no ambiguity as to what level of validation had been applied to each specific subset of data.

Element 12: Data Provision

Data Provision refers to the distribution of data, whether to the public, to university scientists, to regulatory agencies, or to whomever. The form and format of the data depends on the specific needs of the persons to receive the results. Thus, the lay public will benefit from simplified data presented in visual form whether photographs, graphics, or maps. Scientists and regulatory agencies will benefit from data presented in machine-readable form for easy input into geographic information systems (GIS) or statistical software packages. It must be kept in mind that the term data includes not just measurements made on collected samples, but also all ancillary QA/QC results.

Graphics often can be used to communicate complex data sets with clarity, precision, and efficiency. Graphics are intended to reveal patterns in data, often being more revealing than lengthy tables of numbers resulting from statistical computations. The principles of graph construction are: (1) clear vision, (2) clear understanding, (3) appropriate scales, and (4) general strategy. Clear vision focuses on making the data stand out and avoiding clutter. Clear understanding presents major conclusions in graphical form. Selecting appropriate scales allows comparison of graphs. The general strategy of graphics is to pack a large amount of quantitative information into a small space. Graphs should always stand alone. There should be no requirement to refer to text or external data sets.

The Quality Assurance aspects of the Data Provision element should ensure that three key goals are met. First, the results must be perceived by all parties to be complete and accurate. Second, the results must be perceived as timely. Third, the results must be convenient for users to obtain, understand, and use.

Element 13: Statistical Analysis

The statistical analysis of monitoring data ranges from simple hypothesis testing through sophisticated time series analyses and forecasting techniques. Three important points to keep in mind are that good statistics won't fix bad data, that bad statistics will misinterpret good data, and that the primary goal of statistical analysis is to communicate information. Often, simple techniques of analysis are the most effective; for example, a far wider audience will understand percentages than Z-scores, yet the informational content is similar for a number of purposes. Table 1 identifies a number of statistical techniques for analysis of survey (spatial) and monitoring (temporal) data, and different classes of statistical techniques needed to analyze data. In either case, the recommended approach is that of hypothesis testing rather than data exploration, since hypothesis testing directly ties into the study goals. Our experience suggests that hypothesis testing encourages proper project planning while data exploration encourages a more laissez faire attitude. However, it is vital that hypothesis testing always include consideration of beta, the probability of making a Type II error when null hypotheses are rejected. Peterman (1990) reported that 98 percent of papers in fisheries and aquatic sciences omitted the beta information. Millard (1987) reported that there is widespread misuse of statistics in environmental monitoring, and recommended that professional statisticians be more regularly consulted.

Special care and attention must be paid to statistical assumptions; for example, many procedures require that data observations be both independent and normally distributed. Problems related to data censuring, to pseudoreplication, and to autocorrelation are fairly commonplace. Where violations of statistical assumptions do occur, they must be stated and

TABLE 1. Classes of Statistical Techniques Recommended for the Statistical Analysis of Monitoring (time series data) and Survey (inventory data) Information.

Type of Analysis	Monitoring (Temporal Data)	Surveys (Spatial Data)
Location	Moving Average	Mean, Variance
Loading/Mass Transport	Difference Analysis	Difference Analysis
Events	Outlier Tests, Wavelets	Rare Event Analysis
Water Quality Criteria	Exceedance Testing	Distribution Analysis
Spatial Patterns	Ranking	Cluster Analysis
Environmental Impact	Intervention Analysis	Paired Stations Studies
Patterns for Biota	Species Diversity Comparison	Cluster Analysis
Cyclic Patterns	Spectral Analysis	Pattern Analysis
Trend Assessment	Time Series Analysis	Analysis of Variance

appropriate statistical techniques used. Nonparametric tests can be used for data sets which are heavily skewed or which contain significant proportions of censored data. Heavily censored data require special methods of statistical analysis (e.g., Gilliom and Helsel, 1986; Helsel and Gilliom, 1986; Helsel and Cohn, 1988). The authors believe that the best mechanisms to ensure appropriate statistics are employed include independent audit by a professional statistician plus peer review through publication in refereed journals.

Element 14: Reporting

Reporting must focus on the synthesis of the data collected, not upon the reporting of the data per se. It is crucial that interpretative reports provide the broad view environmental situation necessary to communicate effectively with managers, politicians, and the public. The understanding and reporting of environmental quality on the basis of processes, events, and mechanisms (rather than individual data results) is the most effective method of communicating with these diverse audiences. Cullen (1990) notes that decision makers prefer reports which are concise, which make explicit recommendations, and which clearly identify key variables. While it is important that scientists studying environmental quality phenomena understand the fine detail of events and observations, nonetheless, many people who will encounter the published reports will be nonscientists. Therefore, understandable summary-type explanations should be emphasized. Short, simple interpretive reports accompanied by one or more thick detailed technical appendices can be both practical and cost effective. The short reports can be widely distributed at minimal cost, while the detailed information is available for scientists. Cullen (1990) also makes the important point that conflicting advice from otherwise credible sources tends to be disregarded.

Interpretive Reports should provide a synthesis of the accumulated data, including ancillary QA/QC results, and should also recommend future actions. This process can go on in a number of modes: process identification, problem solving, and attainment of desired effects. The synthesis of the data collected must be targeted to the specific goal for which the data were collected. For ongoing studies, Interpretive Reports must be issued on a regular basis to assure that program goals remain current. These updated goals then become the basis for the Design element of the next iterative cycle. It should always be kept in mind that the primary purpose of a report is to communicate information to some audience. Therefore, the information must be assembled in a well-organized fashion so that a person may conveniently review the results. Take the example of a situation where 30 variables were analyzed at a site once a month for one year. If the results were reported with one page of results for all 30 variables for each sampling date, then a person looking for seasonal trends would be flipping pages back and forth. However, if the results are presented as chronological data sets or

as chronological plots, then a person can readily scan the results to check for outliers, patterns, and trends.

The quality assurance for the Reporting element has four main goals: (1) to ensure that interpretive reports are issued on a timely basis, (2) to ensure that the findings are understandable to a diverse public readership, (3) to ensure that the presentation is relevant to known environmental problems, and (4) to ensure that the overall program from start to finish is credible to other scientists. This last aspect of QA is best answered by ensuring that both the overall program and key elements to it are independently reviewed by publication in refereed scientific journals. Additionally, the QA Protocols for the Design element of the following cycle must ensure that results from the interpretive reports are used as the basis for modifications to the next series of Project monitoring programs.

SUMMARY

It is the authors' opinion that quality assurance procedures must be applied to all aspects of environmental studies, from project design through reporting. Yet, according to our experience, the majority of studies focus QA efforts primarily upon laboratory operations with some secondary effort regarding sample collection and handling, but with little QA effort for other aspects. Our strategy towards encouraging more comprehensive programs of QA is to define major projects as repeating cycles of 14 discrete elements, with each element having its own unique program of quality assurance. This model additionally can be used to present key QA-relevant features of a complex environmental study, simply and on a single page (see Figure 2 for an example presentation of the overall QA features for the Canada-British Columbia Water Quality Monitoring Agreement Study). This study has been detailed elsewhere (Anonymous, 1992; Clark, 1992). One can scan a figure and readily identify the program weaknesses; namely, lack of formal protocols and audits in the last six elements. Also, the last peer-review of the overall project Design was some seven years ago, and is no longer current. Conversely, the project does have some strengths – namely, encouragement of peer-review plus formal protocols or published procedures for a majority of elements.

Some quality assurance activities apply to every element of environmental studies, whether or not our model is adopted. Activities must be designed to meet the formal goals of the study, and must not be done on an ad hoc basis. Protocols and procedures must be published and kept current. All personnel must be thoroughly trained and every staff member, no matter how senior or junior, must be assigned definite QA responsibilities. However, one person should be designated to hold primary QA responsibility for any activity. Records must be kept on a formal basis, kept current, and protected from loss. At the conclusion of a project, all documents and records should be sent to a permanent archive. Activities must be audited on a regular basis, and at least occasionally by an independent party. Exceptions from scheduled activities or routine scenarios must be recognized as commonplace, and appropriate contingency plans developed. Scientific credibility must be maintained through cross-agency QA/QC, external audits, and peer review. Proactive and negative feedback approaches must be encouraged so that unacceptable deviations from QA are prevented or identified on a timely basis. Retrospective approaches to QA gamble that major portions of the collected information might have to be discarded.

Our experience suggests that, if less than 30 percent of the overall budget is allocated for QA, the quality assurance programs are unlikely to be adequate. Some situations will call for over 50 percent of budget for QA, particularly where there are major flaws in procedures, methods, or equipment to be corrected. Administrative managers may be unsympathetic to the considerable costs of quality assurance and it is wise to emphasize cost-benefit ratios, and also the fact that the QA program for a major study will extend considerable spinoff benefits to an organization's regular operations. Bad data for half the price of good data is a fool's investment.

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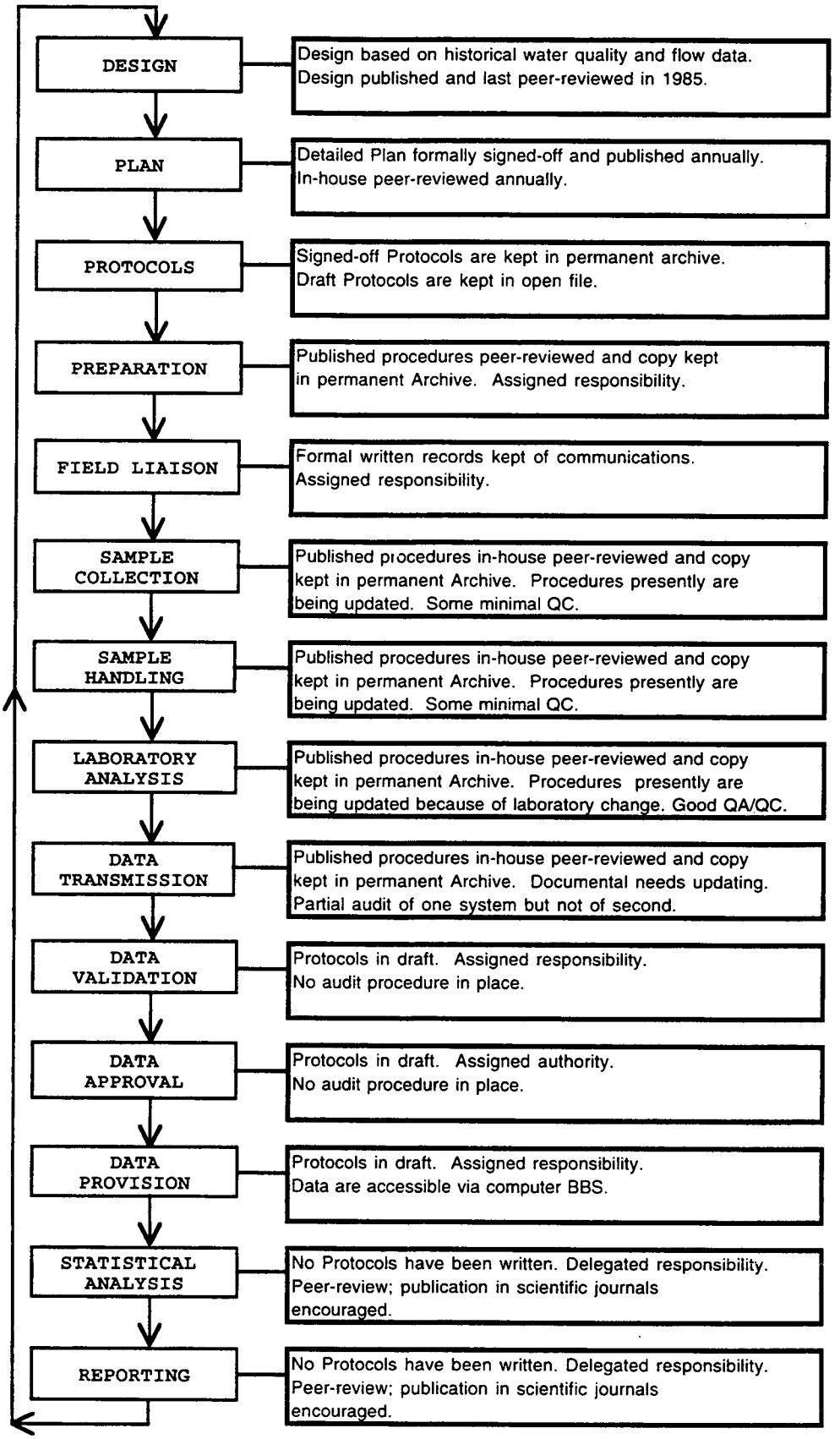

Figure 2. Demonstrative Use of the Iterative Cycle Model to Present Key Quality Assurance Features for Environmental Monitoring Implemented Under Terms of the Canada-British Columbia Water Quality Monitoring Agreement.

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CALCULATING MDC'S

TOWARDS A UNIFORM APPROACH

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CALCULATING MDC'S - TOWARDS A UNIFORM APPROACH
TEXT

Dorothy A. Jeffery

[Italics text is in text but not in talk]. Printed Oct 25/93 8:30 am

1. Many definitions, many terms

1a. I will limit the number of concepts presented, and tend to use DL most frequently.

The aim is to try to understand the concept not remember the name.

2. The definition include:
   - DL EPA
   - DL Keith
   - IDL
   - MDL
   - LOQ

   exclude: PQL, (see Std Methods 18:1030E, 1010C, & Keith)

Some introduction:

3a. (the EPA definition of DL)
-a reported value is often viewed as "a" value
-a detection limit is seen as a defined line, either the analyte is there, or it is not.

-in reality both the value and the DL are a range
-whether you can detect a concentration depends more on the variability of the measurement than the height of the signal.

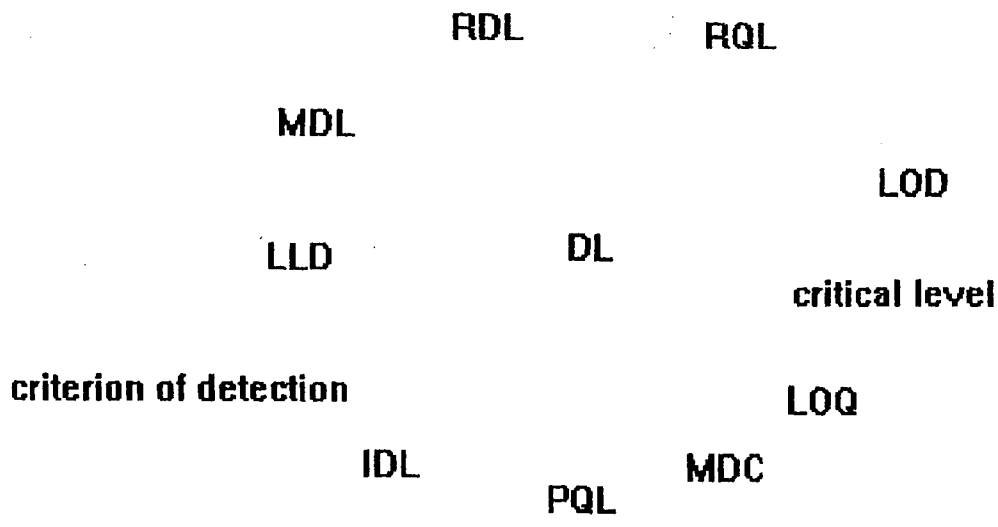
-Keith Fig 9, shows the normal distribution for a true analyte value of conc.=0.
Note units in standard deviation on the "X" axis, in order to make the diagram more broadly applicable.

"Y" axis increasing probability, units could be assigned .....

the "normal" distribution
centered on "0"
symmetrical
if units were assigned, you could see that the area under ± 3 SD = ~99% of the area
± 2 SD = ~95% of the area
± 1 SD = ~68% of the area, giving the curve its shape.

If we make multiple measurements of analyte concentration, we see that half the time we see measurable concentrations of the analyte, even though its true concentration is "0".

By deciding that we are willing to accept some risk of declaring a concentration true when it is not, we can set a concentration where it can be distinguished from "0". This is essentially a detection limit, a level at which we have a known certainty that a concentration is different from "0".


RDL
RQL
MDL
LOD
LLD
DL
critical level
criterion of detection
LOQ
IDL
MDC
PQL

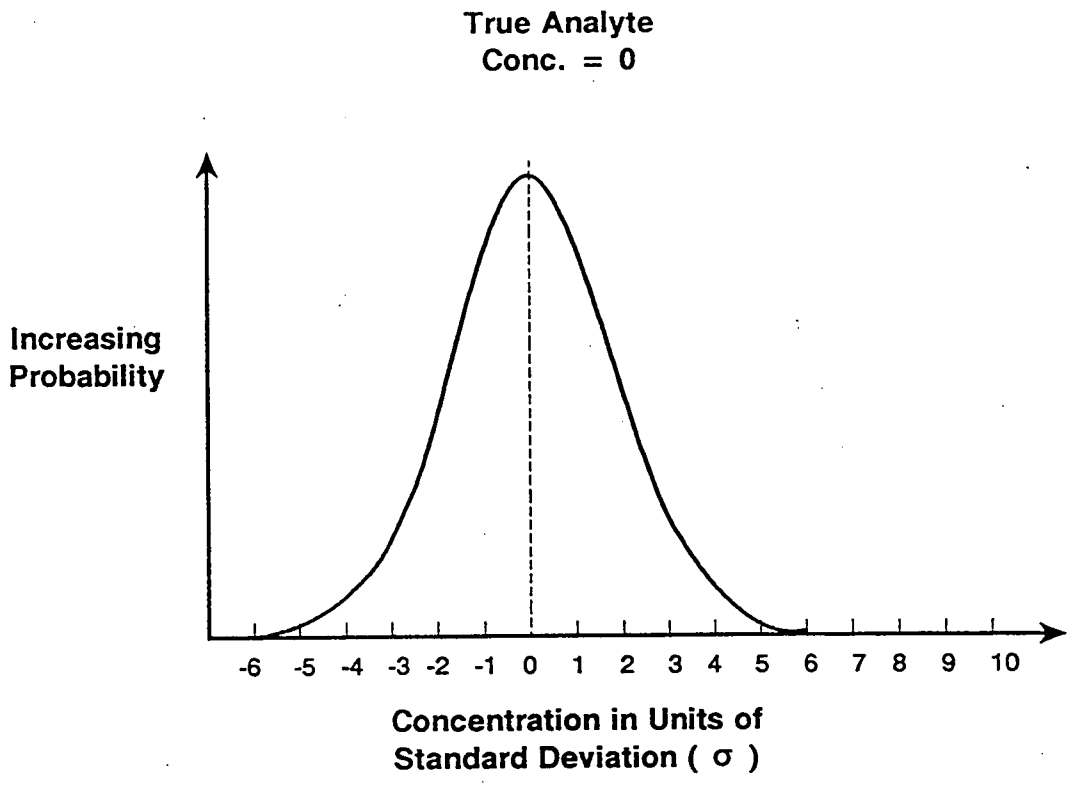


Figure 9. Graphic representation of a PDF curve, where the true value of an analyte is zero.

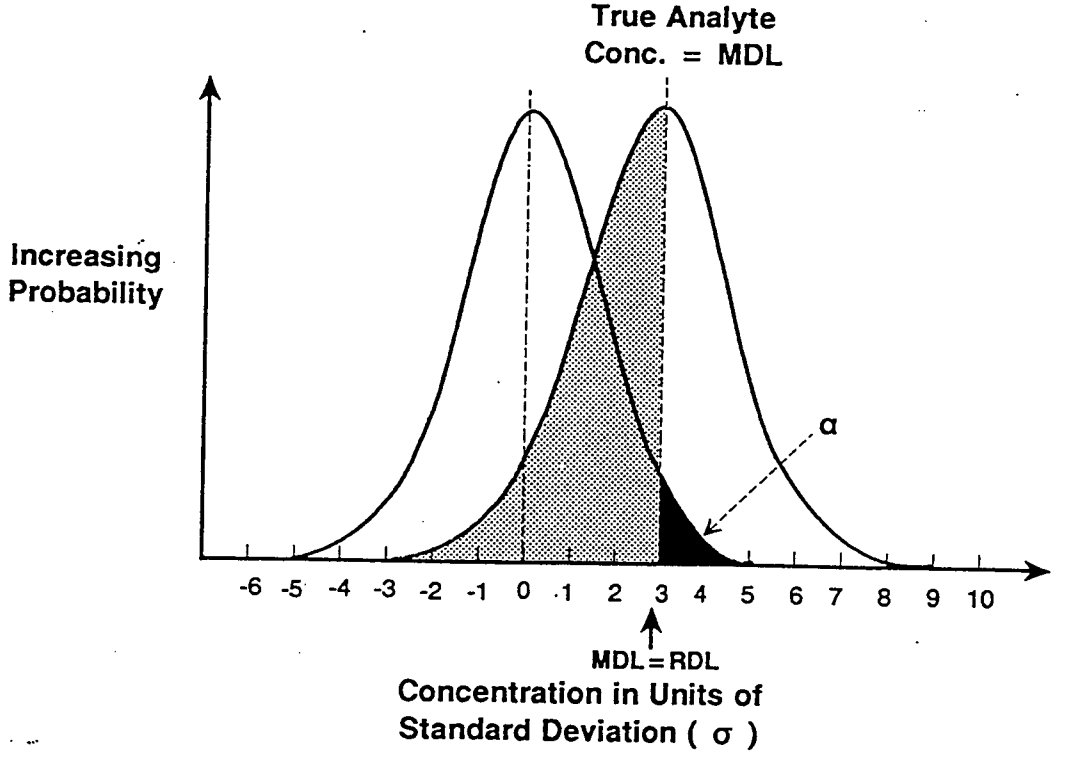


Figure 10. Graphic representation of an unbalanced false positive/false negative risk when the MDL and the RDL are the same.

The frequently used definition of detection limit (Federal Register 40CFR .....), which I will call the EPA definition, uses the 3σ definition. Thus, if a concentration is greater than 3σ above "0", there is >99% probability that a measured concentration is greater that "0". <u>The analyte has been detected.</u>

Conversely there is <1% chance that the analyte is NOT present.

I'll look at the underlying assumptions and some practical considerations about this definition later, but first I'd like to go onto another frequently asked question when low level analysis is done.

3b. (The Keith definition of DL)

For people doing environmental monitoring, or required to meet permit levels, the question often asked is "This result is <DL. Does that mean there is nothing there?"

What does our "EPA" definition say about this. Not a lot.

If we take our distribution and move the central point up to set a detection limit at 3σ (Figure 10), we know there is some analyte there, *but in 50% of the observations (measurements), the result will be below the detection limit. This means the analyte was not detected, even though we know it is there.*

Figure 10 shows that when detection limit is set at 3σ, <1% of the time when analyte concentration is "0" will we say that some analyte is present (the black portion of curve labelled α). *Alpha is the probability of a Type I error (saying something is true when it is not: specifically saying the analyte is present when it is not).*

The gray portion of the graph shows that if the true concentration is in fact = 3σ, 50% of the time we will say it is not there. The gray portion labelled β is the probability of a type II error *(saying something is not true when it is: specifically* ,saying the analyte is not present when it is).

In order to reduce the size of the type II error, we can raise our detection limit. [Figure 11 Keith & leave on]. Incidentally we further lower the probability of the type I error.

Remember that the distribution centered on "0" gives the α probability, and the distribution centered on the detection limit gives the β error where the 2 distributions intersect.

By setting the detection limit 2 x 3σ ($=6\sigma$), we have <1% chance of a type I error (saying the analyte is present when it is not), and 1% chance of a type II error (saying an analyte is not present when it is). This is a much more balanced situation, than the "EPA" definition (<1% chance of type I error, but 50% chance of type II error, failing to see an analyte that is present).

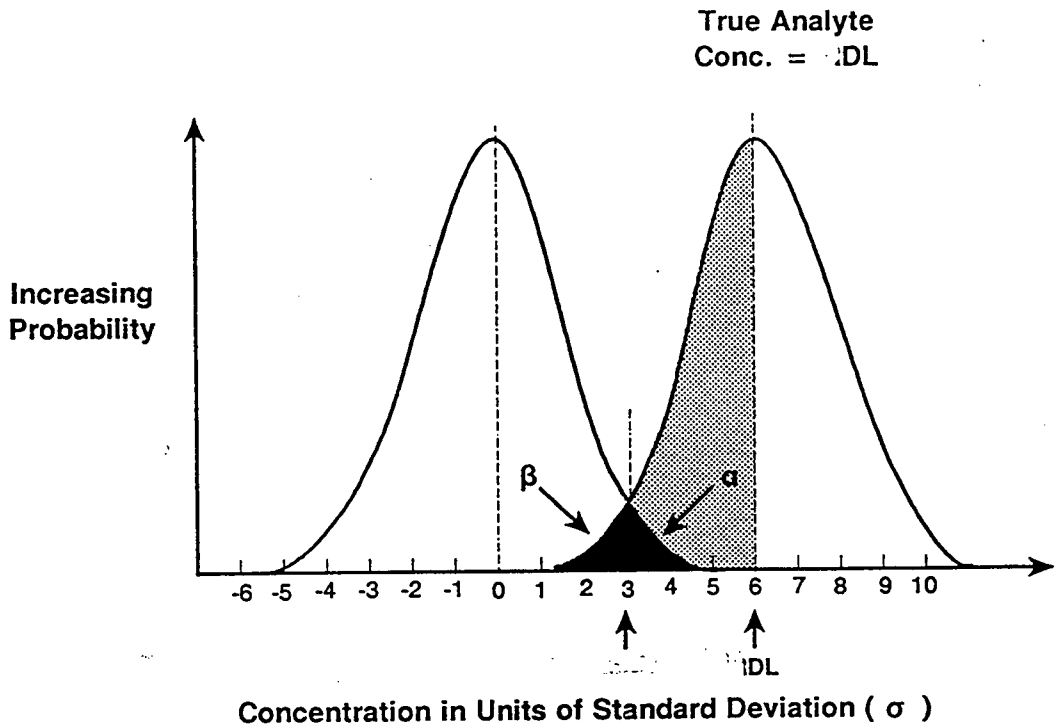


Figure 11. Graphic representation of the MDL and the RDL, where false positive (α) risk and false negative (β) risk are equal, and each is less than 1%.

CAEAL has adopted this definition, but has defined the detection limit with 95% confidence that the value is different from "0", which is 1.645 σ. When both the α and β confidence limits are set at 95%, the CAEAL detection limit becomes 2 x 1.645 σ = 3.29 σ
with the probability of both α and β errors at $\leq$ 5%.

[Have Table 3 available, but probably do not use].

Now that we have two definitions of detection limits, lets look at some of the underlying assumptions, as a type of review.

3. The underlying assumptions

3a. Frequently not recognized

3b. Frequently not tested

3c. Re distribution

3c.i Normal distribution

One of the underlying assumptions of these DL calculations is that the data used to estimate the DL is normally distributed.

This assumption is often not confirmed.

The distribution may be flattened, so the % of area enclosed by say ± 3 SD is less than 99%.

The distribution may be skewed to the left or the right. This can be shown to the case for some/much blank data.

When the criteria for the normal distribution is not met the probabilities of errors will differ from those described in the theory.

3c.ii. the infinite population

The theory presented so far has used sigma, the population statistic for standard deviation. It is not possible to known the standard deviation of an entire population of environmental data.

3c.ii. the finite sample

Correction can be made for the finite sample size used to estimate standard deviation.

The 't' distribution is the normal distribution adjusted for sample size.
For the determination of detection limit, we use the 'one-sided' part of the table because we are interested in only one side of the distribution [Figure 10 or 11]. We only want to know the probability that the true value is greater than the limit we have set. (We do not care about the other tail of the symmetrical distribution).

Table 3. Probability of False Positive/False Negative Determinations

MDL or LOD	RDL	False Positives [α]	False Negatives [β]
3σ	3σ	0.1%	50%
3σ	4σ	0.1%	16%
3σ	5σ	0.1%	2.3%
3σ	6σ	0.1%	0.1%
2.33σ	2.33σ	1%	50%
2.33σ	4.66σ	1%	1%
1.64σ	3.28σ	5%	5%

The 't' value to use with a given sample size varies with the sample size. A partial 't' table follows:

df	α 0.01	α 0.05	one sided 't'
∞	2.326	1.645	
20	2.528	1.725	
10	2.764	1.812	
7	2.998	1.895	
5	3.365	2.015	
3	4.451	2.353	

3c.iii. Type I error (α)

This is the probability of saying an analyte is present when is not, or declaring a false positive. This has been discussed already.

For the 'EPA' definition the probability of a Type I error is <1%.

For the 'CAEAL' definition the probability of a Type I error was set at 5%, actually <5%.

3c.iv. Type II error (β)

This is the probability of saying an analyte is not there when it is. That is it is the probability of a false negative.

The 'EPA' definition does not recognize the probability of a Type II error, but the probability is 50%.

The 'CAEAL' definition recognizes the Type II error and sets the probability at 5%.

3d. re blank

The 'EPA' definition states blank level should be measured on every sample used to determine the MDL, if blank correction is required in the analytical procedure. *The average blank should be subtracted from the sample measurements used to determine MDL.*

The 'CAEAL' definition refers to data being appropriately blank corrected if necessary.

Guidance on 'appropriately blank corrected' is necessary.

3d.i. blank distribution

3e. The formulae for detection limits for n=infinity are

EPA: DL = 3σ with 99% confidence on α only,

CAEAL: DL = 2 x 1.645σ = 3.29σ with 95% confidence on α & β.

Formulae for detection limits for n=infinity

EPA: DL = 3σ with 99% confidence on α only,

CAEAL: DL = 2 x 1.645σ = 3.29σ with 95% confidence on α & β.

4. Who is using/promoting the definition

4a. MDL -1984 EPA definition -original 40 CFR Part 136, October 26, 1984 Federal Register Part VIII. (40 CFR Chapter 1 (7-1-90 Edition Part 136, Appendix B. - current version).

The first definition I described, has been used in the US on a regulatory basis since 1984 . Its use has been criticized throughout by various people. Much discussion has taken place.

4b. RDL - L Keith, Radian, CAEAL, maybe BC MOE (QA task group/new methods manual).

The second definition I gave, which recognizes both the type I and type II error probabilities, was introduced in 1990 by L. Keith, and promoted since then but not yet to success in the US. It has been adopted in Canada by CAEAL, and maybe the BC MOE (in the new methods manual). CAEAL is a step ahead in using this definition, in my opinion. (Being a step ahead necessitates being out of step, but I can show , the additional effort involved in recognizing the two definitions is not large). [Formulae slide , an extra line of text].

You will have noticed that when I discussed the "EPA" definition, I used 3σ (<1% chance of type I error), but when I discussed the second definition, I used 1.64σ + 1.64σ (5% chance of a type I error, and 5% chance of a type II error). There are practical reasons in choosing the latter: easier to convince people to accept the second definition. In fact the definitions presented can be applied at many reasonable levels of probability, as long as the level is stated.

4c. **Limit of quantitation-** (LOQ) is less rigorously defined as 10* SD. The LOQ is the concentration at which quantitative results are possible (precision approaches ± 30%). At the MDL, on the other hand, the presence of the analyte is defined with certainty but its concentration cannot be defined (precision ± 100%).

5. The practical side of determining DL

5a. What I see is what you get
-no estimate of variation

5b. Rigidly defined protocol
spike reagent water at conc X and make 8 replicate determinations; calculate using one factor (eg. MISA options c & d, and older EPA definitions ??).

5c. Determining variability data: (see MDC_ZEL) and QAWG documents

Minimum detectable limits (MDL's) *are set at the 95% confidence level above zero (or the blank - see later). For an infinite number of replications this is*

$$MDL = 2 * 1.645 * SD_{near\ zero}$$

$$= 3.29 * SD_{near\ zero}.$$

where SD near zero is standard deviation estimate made within a factor of 10 of the (expected) MDL.

MDL for a smaller number of replicates *is*

$$MDL = 2 * t_{1,0.05} * SD_{near\ zero}$$

where $t_{1,0.05}$ *= the one-tailed 't' statistic at p=0.05 (see Table later).*

The standard deviation, SD, of a low level sample may be used to produce this estimate. The determination of SD must be carried out
(i) on a sample that is stable,
(ii) at an analyte concentration which minimizes the over estimation of $sigma_0$, (the population standard deviation at zero), and yet is sufficient to produce a measured concentration value that is statistically significant (the concentration 1-3 x MDL is recommended).
The standard deviation used to estimate $sigma_0$, may be within batch standard deviations provided by duplicate or replicate samples carried through the same sample processing steps, or duplicate or between batch replicates.
Calculation of standard deviations should be based on
(i) blank corrected data, if appropriate,
(ii) and a sample size of at least n = 7. The 't' statistic is used to compensate for the tendency of small sample sizes to underestimate variability.

Significant Figures:
MDL's should be recorded to one significant figure.
Data used to estimate SD should be recorded to one extra significant figure than data is normally recorded to in order to reduce rounding errors in the SD estimate.
Results should be reported to no more decimal places than the DL.

The formulae used to calculate standard deviation, SD, are as follows:

Case 1. duplicate analyses carried out in successive batches

$$SD=\sqrt{\frac{\sum (x_1-x_2)^2}{2n}}$$

where n= number of pairs of data.

Case 2. replicate analysis carried in a single batch

$$SD=\sqrt{\sum \frac{(\bar{x}-x_i)^2}{(n-1)}}$$

where n = number of replicates.

Case 3. replicate analysis carried out in successive batches

$$pooledSD=\sqrt{\frac{(v_1*s_1^2)+(v_2*s_2^2)+.....(v_i*s_i^2)}{(v_1+v_2+.....v_i)}}$$

where v= degrees of freedom for each batch.

Values of the one-tailed 't' statistic at p=0.05, applied to the standard deviation, SD, appear in the following table:

Degrees of Freedom	$t_{(0.05)}$
7	1.90
8	1.86
9	1.83
10	1.81
15	1.75
20	1.73
25	1.71
30	1.70
40	1.68
60	1.67
infinity	1.64

For case 1, duplicates, degrees of freedom = n the number of pairs of duplicates,

for case 2, replicates in same batch, degrees of freedom = n -1, where n = the number of replicates,

for case 3, pooled SD from replicates in successive batches, degrees of freedom = sum of $v_1 + v_2 + \ldots v_i$.

Examples of samples for estimating SD for MDL calculation (preferred approaches are shown first).

1. Replicate analysis of a bulk sample of the desired matrix known to be homogenous and stable. Sub-sampling of the bulk sample is performed and each sub-sample is carried through the entire preparative and analytical step. Concentration is not to exceed 10 times the estimated MDL, but is preferred to be 1-3 times the estimated MDL. Estimate SD using formula case 2 for single batch analysis, and formula case 3 for multiple batch analysis.

2. If a bulk sample is not available, prepare a composite sample in the concentration range required. Continue as in 1.

3. If above two are not possible use duplicate analyses from several batches, adhering to the described concentration range. Use formula in case 1 for estimation of SD.

4. If above three are not available, use a spiked blank or clean matrix, to produce a large sample. Take steps to assure the spike is homogenously distributed (eg. mixing overnight). Spike to a concentration not greater than 10 times the estimated MDL. Subsample this bulk spiked sample and carry each sample through all preparative and analytical steps. Use formula case 2. to estimate SD.

5. If facilities do not allow preparation of a bulk spike sample, spike individual blank or clean matrix samples to a concentration as defined above. Take steps to assure the spike is homogenously distributed (eg. mixing overnight). Continue as described above.

6. If no blank or clean matrix is available proceed as in 4 or 5 using pure de-ionized water as the matrix.

7. Organics application of 3x noise in the area of the analytical peak can be used if none of the above can be used. This produces an estimate of instrument SD and little of the contribution of preparative and matrix effects.

Examples of samples for estimating SD for MDL calculation (preferred approaches are shown first).

1. Replicate analysis of a bulk sample of the desired matrix

2. A composite sample in the concentration range required.

3. Duplicate analyses from several batches, adhering to the described concentration range. Use formula in case 1 for estimation of SD.

4. Spiked blank or clean matrix, to produce a large sample. Take steps to assure the spike is homogenously distributed (eg. mixing overnight).

5. If facilities do not allow preparation of a bulk spike sample, spike individual blank or clean matrix

6. Spiked de-ionized water as the matrix.

7. 3x noise in the area of the analytical peak This produces an estimate of instrument SD and little of the contribution of preparative and matrix effects.

Modifiers

The MDL should be modified to describe how the data was obtained.

Instrument DL - the data for determining the MDL is derived using only the instrument steps of the analysis, eg. a GC analysis of pesticides in water where no extraction step is used in obtaining the MDL data, and only repeated injection of the analyte in solvent would we an instrument MDL.

Method MDL - the data for determination of MDL was obtained by carrying replicate samples individually through all preparative and analytical steps, eg. as above except samples are extracted and analyzed.

Method MDL should be further defined to indicate the matrix to which it applies and matrix upon which it was determined.

Examples are shown:

MDL_{soil} - method MDL intended for use with soil samples and determined on soil matrix,

$MDL_{soil/water}$ - method MDL intended for use with soil samples BUT determined using water matrix,

$MDL_{soil/calc}$ - MDL for soil calculated from the dilution factors of a water MDL.

Additional modifiers could be used for plants, animal tissue, water dissolved, waters total.

It is necessary to accept different types of MDL's because, for example, there may be insufficient sample or no clean matrix to run method MDL's in all situations.

Method MDL should be further defined to indicate the matrix to which it applies and matrix upon which it was determined.

Examples are shown:

MDL_{soil} - method MDL intended for use with soil samples and determined on soil matrix,

$MDL_{soil/water}$ - method MDL intended for use with soil samples BUT determined using water matrix,

$MDL_{soil/calc}$ - MDL for soil calculated from the dilution factors of a water MDL.

6. Interpretation of DL

6a. In today's climate find out what the lab means

6b. Remember the detection limit wars.

6c. What type of error is important to your work?

6d. Remember that limit is not a line, it is a range

Conclusion-

I have recognized that the issue of detection limits is not settled. Much discussion continues. But to be pragmatic, I have chosen to look a only two definitions: the KEITH/CAEAL definition which recognizes and sets a balanced false positive and false negative rate, and the EPA definition which is widely used but is incomplete in its recognition of errors. I favour the former definition.

The second important point is that detection limits must reflect the matrix to which they are to be applied. To the best of our ability we need to obtain data which represents the samples when we estimate detection limits. Finally we must state sufficient information with detection limits to indicate how they were obtained.

7. References/credits

Federal Register, Environmental Protection Agency, 40 CFR Chapter I (7-1-90 Edition), Part 136 Appendix B, p.537-539.

Keith, L, "Environmental Sampling and Analysis, A Practical Guide", Lewis Publishers, Chelsea, Michigan, 1991, pp.95-111.

Taylor, J. K., "Quality Assurance of Chemical Measurements", Lewis Publishers, Chelsea, Michigan, 1987.

MISA, "Estimation of Analytical Method Detection Limits (MDL), report prepared by G. Crawford, Laboratory Services Branch, Ontario Ministry of the Environment, June 1991.

**********the end**********

The issue of appropriate blank correction has not been addressed in this paper.

Blanks 0, < MDL, meaningfully matched, batch blanks.

Case 1 - blank = 0, no adjustment to the MDL calculation is necessary.

Case 2 - blank < MDL, since a value less than MDL cannot be distinguished from zero, no adjustment to the MDL calculation is necessary.

Case 3 - meaningfully matched blanks, can be used to blank correct the data before calculation of the MDL. An example of meaningfully matched blanks are daily digest blanks when batches of data are acquired over several days. Because blanks contribute an additional source of variation, the estimate of MDL will be elevated. The formulae for estimating SD are the same as above. Data for 33 elements in total metals ICP scan showed that for 9 elements the MDL was increased by daily blank subtraction, for 3 elements there was no effect on MDL, and for 21 elements the MDL was decreased by blank correction.

Case 4 - batch blank applied to a single batch of data, does not alter the estimate of SD nor the estimate of the MDL. Subtraction of one degree of freedom prior to choosing the 't' value will elevate MDL slightly. This does not yield an appropriate estimate of the MDL when blanks are non-zero.

ISOMET - CONTAMINATION FREE SAMPLING

Robert C. McCrea

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Ontario Region

An Assessment of the Pukaskwa Water Sampling Program: Review of Replicate Data and Performance of the ISOMET Stream Sampler

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Abstract

The ISOMET stream sampler program was developed by the Water Quality Branch, now known as the Ecosystem Health Branch, to provide reliable water quality data, for an assessment of stream chemistry in Pukaskwa National Park. It is intended for use in surface water sampling applications, at a nominal depth of 0.5 to 1m. Sampling materials are prepared in a clean air workstation, and are maintained in clean state throughout the sampling process using simple and effective isolation and containment strategies.

The ISOMET sampling system has proven to be rugged and reliable, under a wide range of stream velocities, and in air temperatures ranging from +35 to -35°C. In terms of data quality, there has been a high degree of correspondence within multiple replicate sets for trace metals, sampled in a wide range of environmental concentrations.

Introduction

Monitoring of trace metals in surface waters has been fraught with considerable uncertainty owing to severe contamination problems. As detection limits and more appropriate quality assurance and quality control protocols have been developed, it has become evident that much of the historical freshwater are suspect. Recently, considerable mitigation of these problems has been achieved through use of portable field laboratories. Many of these developments, however, are not suitable for remote monitoring applications where transportation is limited, and where access is difficult.

The ISOMET stream sampler was designed to provide reliable trace metal samples for a monitoring program in Pukaskwa National Park (PNP). Pukaskwa is a wilderness park, located along the northshore of Lake Superior, in one of the more rugged regions in Ontario. With few exceptions, Pukaskwa's streams and lakes are only accessible by helicopter.

The approach adopted in the development of the PNP monitoring program was to design a portable sampling system, of modular design, where the risk or occurrence of contamination would be mitigated through the use of isolation and containment strategies. The resulting ISOMET sub-surface sampler and related protocols were developed for sampling streams during both open-water and under-ice conditions.

As an integral part of the PNP stream and lake monitoring program, a series of blank and replicate samples were collected to obtain a measure of the precision and accuracy of the data being generated. These quality control data are summarized in this report with a particular emphasis on the trace metal data sets. In addition, information regarding the suitability and appropriateness of the sampler under a wide range of field conditions is presented.

Method

The ISOMET stream sampler consists of three basic components: a rod, body and bottle/valve assembly (Fig. 1). Of these, the bottle/valve assemblies are most critical since they come in contact with the water being sampled. All sample bottles and sample processing materials, including the valves and bagging, are routinely prepared in batches in a laminar flow work station, where they are subjected to a 5-step cleaning procedure. Immediately following cleaning, sets of bottles and valves are assembled as a kit, and then double bagged to maintain their integrity through the life-cycle of the monitoring process. Bottles from each batch processed are randomly chosen as preparation blanks and are verified prior to being shipped to sample collectors. A complete description of the sampler and related protocols can be found in McCrea and Fischer (1994).

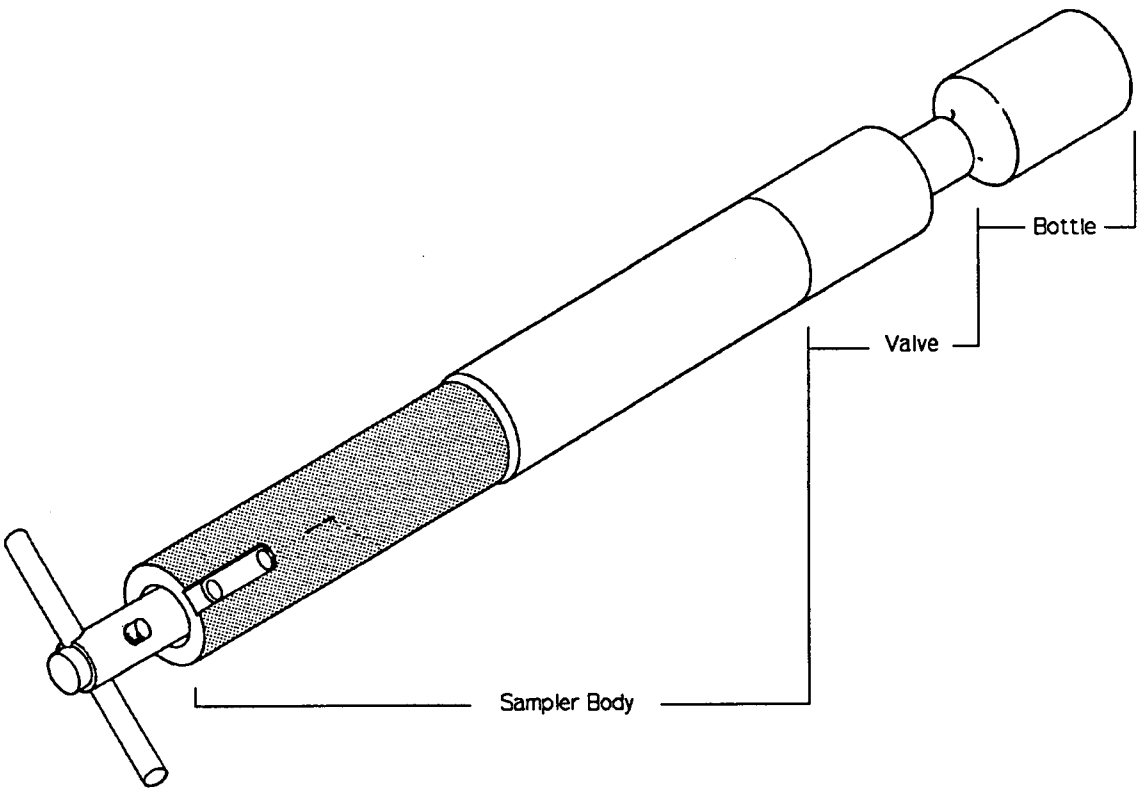


Figure 1. An illustration of the ISOMET stream sampler.

In the field, sampling personnel thread the bottle/valve assemblies to the sampler body without removing the double bagging. Immediately prior to sampling, the bagging is carefully removed and the sampler is lowered, in a closed state, into the water. The lower end of the sampler is then whisked through the water for one minute with the bottle/valve assembly pointing upstream. Once rinsing has been completed, the valve is then opened underwater. After the sample bottle has filled, the valve is closed and the ISOMET is withdrawn from the water body. The sample bottle is immediately double bagged, and placed in a plastic shipping case to maintain the integrity of the sample.

To mitigate contamination, the samples are forwarded directly to the trace metal analyst for the National Laboratory for Environmental Testing (NLET). While under the custody of the analyst, the bottles are kept in their double bags, and sealed in shipping cases until time of analyses. The samples are concentrated, and later analyzed with an Inductively Coupled Argon Plasma - Optical Emission Spectrometer (ICAP-OES).

Results

Physical Appropriateness

In terms of the appropriateness of a water sampling system, it is important that all components expected to come in contact with the water being sampled are:
1) suitable for the application, including the range of air and water temperature, and are appropriate for the nature of the water body being sampled;
2) non-contaminating; and,
3) easily maintained in a clean state through the life-cycle of the sampling process.

Preparation of bottles, valves, and other materials for the ISOMET sampling program, has proven to be very reliable. In 3 years of sampler use, all preparation bottle blanks have been shown to be effectively free of contamination.

The ISOMET has been deployed in a wide range of environmental conditions and in temperatures ranging from +35 to -35 °C. The sampler has been used successfully to collect samples during open-water conditions from boats, canoes, off helicopter pontoons and by wading. It has also proven to be effective for sampling water below ice cover. Problems associated with both stagnate water which may contain melt waters from the ice pack having a much different chemical profile and with possible contamination resulting from cutting the sampling hole have been averted. As a result, representative water samples of free flowing water under ice cover have been routinely obtained.

Despite the fact that the sampler is of relatively light weight, it has proven to be rugged and durable, and can withstand the stress of high flow conditions. Not a single sampler has been lost to date - it floats.

The ISOMET is shipped in a rigid protective casing and, to date, there has been no incidents of breakage. Subsequent to its deployment in Pukaskwa National Park, the ISOMET has also been deployed successfully used in numerous locations throughout Ontario, including streams in the James and Hudson Bay frontier.

Data Validation

Multiple replicate sets were obtained during lake surveys, and serial replicate sets were collected as part the stream monitoring program, for data quality assessment purposes. The first set of lake replicates (N_{rep}=10) were collected, in 1989, from Lake Superior approximately one kilometre off the PNP shoreline (Table 1). Analyses of these whole-water replicates yielded low trace metal concentrations; only Al, Ba, Fe, and Sr had mean values above 1ppb. In all cases, the standard deviation was small, and included variability associated with the natural heterogeneity of the water body as well as analytical variability.

Table 1. A statistical summary of replicate data (N_{rep}=10) from Lake Superior off the Pukaskwa National Park Shoreline.

Parameter	Detection Limit ug/L	Mean ug/L	Standard Deviation
Al	2.	15.2	1.6
Ba	0.2	9.5	0.1
Cu	0.2	0.96	0.1
Fe	0.4	14.5	0.7
Li	0.1	0.7	0.1
Mn	0.1	0.8	0.1
Sr	0.1	22.7	0.3

Note: Concentrations of Be, Cd, Co, Cr, Mo, Ni, and Pb were at or below their respective detection limits.

In 1991, a lake monitoring program was initiated, within PNP, to characterize water quality and to assess their sensitivity to acidification. All samples were collected, by PNP staff, off the pontoon of a helicopter. Despite the fact that PNP lakes are susceptible to acid stress, concentrations of many of the trace metals investigated were below 1ppb. Results are presented in Table 2.

Table 2. Median concentration of trace metals in whole water samples from 58 Lakes in Pukaskwa National Park (1991 and 1992), found below 1ppb.

Metal	Detection Limit ug/L	Median Concentration ug/L
Cu	0.2	0.3
Cd	0.1	<0.1
Co	0.1	0.1
Cr	0.2	0.2
Li	0.1	0.4
Mo	0.1	<0.1
Ni	0.2	0.2
Pb	0.2	<0.2
V	0.1	0.2

Standard deviation and other statistical computations for Cu, Cd, Co, Cr, Li, Mo, Ni, Pb, and V were not determined owing to the fact that concentrations were near their respective analytical detection limit, and further statistical analyses would have not been meaningful. The non-detection of these metals does, however, provide further evidence that the ISOMET isolation and containment strategies are effective, for this level of analyses and assessment.

Concentrations of Al, Ba, Fe, Mn and Sr were consistently above 1ppb, and samples were representative of a wide range of environmental concentrations. Results of the replicate data, for metals having concentrations above 1ppb, are summarized in Table 3.

Table 3. Percent coefficient of variance for trace metal replicate samples (N_{rep}=5) collected from four PNP lakes, October, 1991 and 1992.

Metal	Coefficient of Variance (%) Min	Max	Mean	Range of Sample Concentrations (ug/L)
Al	0.32	2.56	1.40	104. --- 676.
Ba	1.12	2.69	2.05	6.8 --- 14.6
Fe	0.81	4.07	2.16	92. --- 290.
Mn	0.41	2.12	1.02	10.4 --- 27.4
Sr	0.62	1.69	1.10	7.1 --- 16.6

Results of the replicate analyses revealed little variation within each set of lake data. Overall the mean %CV for the individual metals ranged from 1 to 2%. It is important to note, that these whole water lake samples were collected when the lakes were essentially isothermal, and when algal concentrations would have been insignificant. Higher %CVs would be expected in whole water samples collected in the summer months when the surface waters exhibit a greater degree of heterogeneity. Much of this variability would not be attributable to the sampling system used.

As part of the stream monitoring program, in PNP, water samples were collected, on a monthly basis, upstream of the confluences of the West and East Pukaskwa Rivers. The West Pukaskwa site was designated as a master station, and replicates were collected at all sampling events, within 5 to 10 minutes of sample collection. Samples and replicates for whole and filtered water analyses were processed within six hours of collection, in a laboratory located in the PNP administration building. Results of these analyses provided a continuous record of data quality. All sample collection and processing was conducted by park staff and, over the period, of record several wardens were involved.

During the development phase of the ISOMET sampler, modifications were made to maintain or improve the effectiveness of the isolation and containment strategies. The West Pukaskwa replicate data set, presented in this report, commences with the first sample set collected from the West Pukaskwa and extends through the development phase and includes data obtained during the deployment of the original prototype.

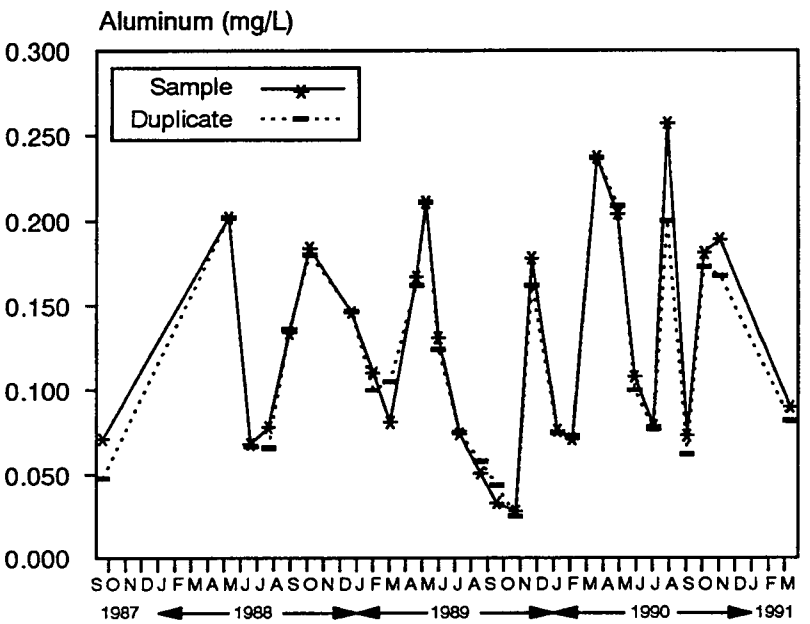
As expected, very good agreement between the sample and replicate data was found for the most abundant major ions, which included calcium, magnesium and alkalinity. Good agreement was also obtained for trace metals such as aluminum, which was present at concentrations approximately two orders of magnitude below that of alkalinity. Aluminum and alkalinity represent two of the most important parameters in the PNP studies. The correspondence between the sample and replicate data sets are presented in Figures 2 and 3, respectively.

Aluminum concentrations varied approximately a 10 fold (Fig. 2). Nonetheless, the mean of the replicate samples was within 4% of the sample mean over this range. There was also good agreement between the individual data points as shown in the time plot and in the sample versus replicate plot. The correspondence of the sample and replicate data for aluminum was only slightly less than that found for alkalinity (Fig. 3).

Of the trace metals consistently detected above 1ppb, manganese and strontium had the highest degree of correspondence between the sample and replicate series. The degree of correspondence was found in the following order: Mn > Sr > Ba > Fe > Al. The correspondence of Mn, Sr, Ba and Fe and the major ionic constituents are presented, in order of decreasing concentration, in the appendix.

The Pukaskwa River monitoring program has also yielded interesting temporal profiles. Despite 5 to 10 fold changes in their concentration, many of the parameters exhibited virtually identical chemical signatures for the West and East Pukaskwa Rivers, over the period of record. This concurrence in water chemistry is attributable to the Pukaskwa watersheds being located in the same ecodistrict, and having essentially the same surficial area. Additionally, both watersheds are unimpacted direct sources of anthropogenic pollution. The detection of this concurrence, particularly for the trace metals, is attributed to effectiveness of the ISOMET stream sampling program.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.125	0.120
Standard Deviation (mg/L)	0.065	0.061
Coefficient of Variation (%)	52.0	50.8
Difference of Means (%)	4.08	



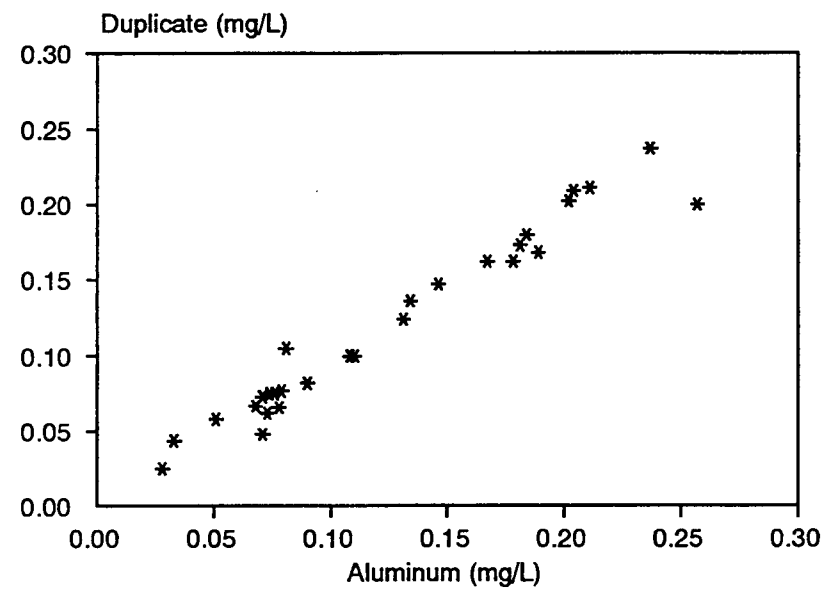
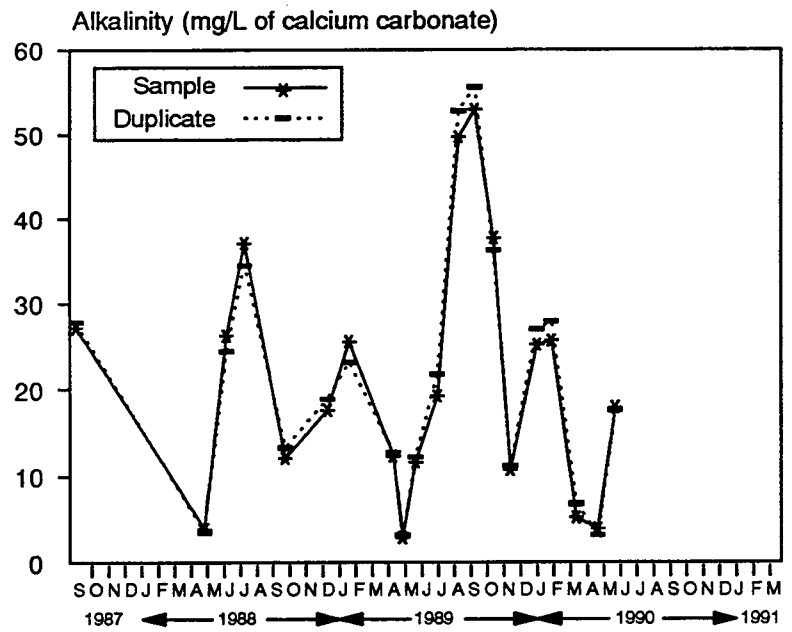


Figure 2: A graphical and statistical summary of aluminum in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	21.2	21.7
Standard Deviation (mg/L)	14.6	14.9
Coefficient of Variation (%)	68.9	68.7
Difference of Means (%)	2.33	



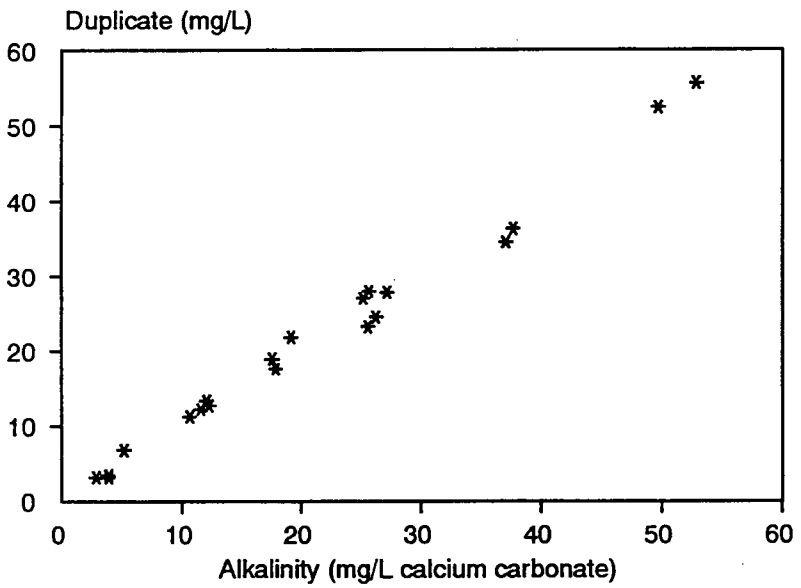


Figure 3. A graphical and statistical summary of alkalinity in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Conclusion

The ISOMET has been successfully deployed over a four year period in Pukaskwa National Park, and in some 15 other monitoring sites located throughout Ontario. The sampler has proven to be rugged and durable, and appropriate for use from boats, canoes, off helicopter platoons, and by wading. It has also been successfully deployed in a wide range of environmental conditions, and in temperatures ranging from +35 to -35 °C. Given that the ISOMET sampler floats, the risk of loss in the field has been insignificant.

Through the use of effective isolation and containment practices, and comprehensive QA/QC protocols, precise water quality data has been routinely obtained. Results of replicate sampling from Lake Superior has illustrated the reproducibility of trace metal sampling with the ISOMET stream sampler, in the lower range of levels found in the environment. The serial replicate data set from the West Pukaskwa River and the multiple replicate data from the PNP inland lake studies have demonstrated the high degree of correspondence possible, over a wide range of environmental concentrations.

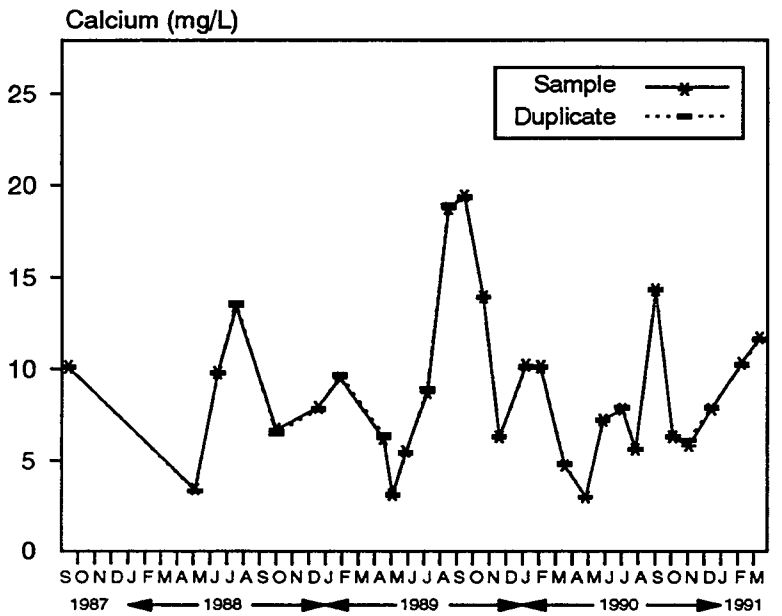
The quality assurance program has been effective in the delivery of data, appropriate for environmental assessments. It has allowed for the routine collection of representative samples by warden staff at PNP, and by numerous lay collectors at other sites in Ontario. Given that the ISOMET sampler and related protocols have facilitated the collection of quality samples by non-water-quality-staff, considerable savings have been achieved in both travel cost and person-years in comparison to more traditional sampling strategies.

Acknowledgements

Special thanks are extended to Chip Bird, Frank Burrows, Dan Couchie, Greg Fenton, Gary Fellbaum, Doris Odjick, Adam Moreland and Charlie Ristau for their support in the Pukaskwa sample collection program; Mary Lou Archer for preparing the sampling material; John Fischer for his support, advice and participation in the PNP monitoring program; Natalie Schito for preparing figures; and, Z. John Licsko for reviewing the manuscript.

APPENDIX

Statistical Profile	Sample	Duplicate
Mean (mg/L)	8.8	8.9
Standard Deviation (mg/L)	4.2	4.2
Coefficient of Variation (%)	47.7	47.2
Difference of Means (%)	1.13	



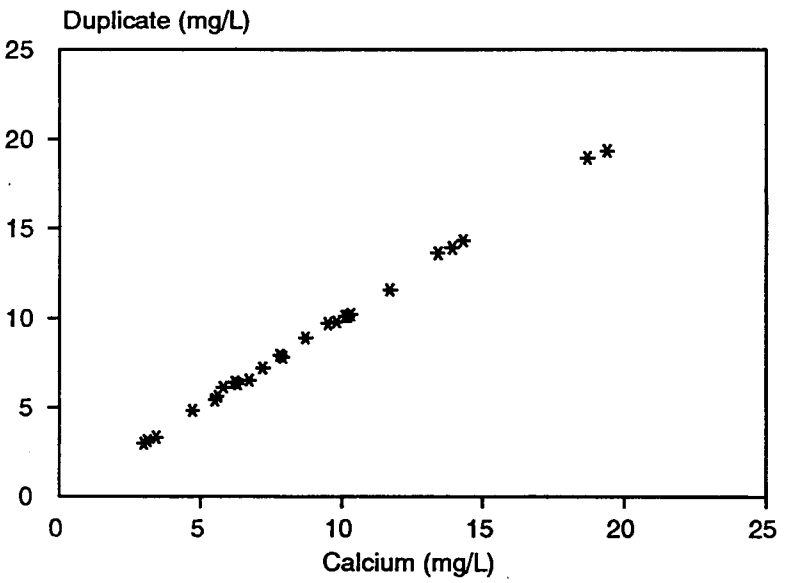
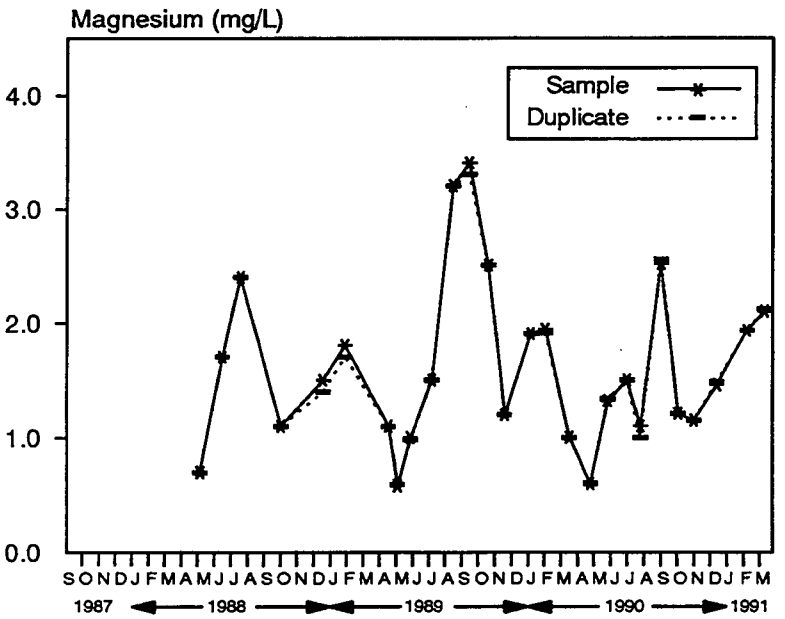


Figure A.1. A graphical and statistical summary of calcium in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	1.61	1.59
Standard Deviation (mg/L)	0.72	0.72
Coefficient of Variation (%)	44.7	45.3
Difference of Means (%)	1.25	



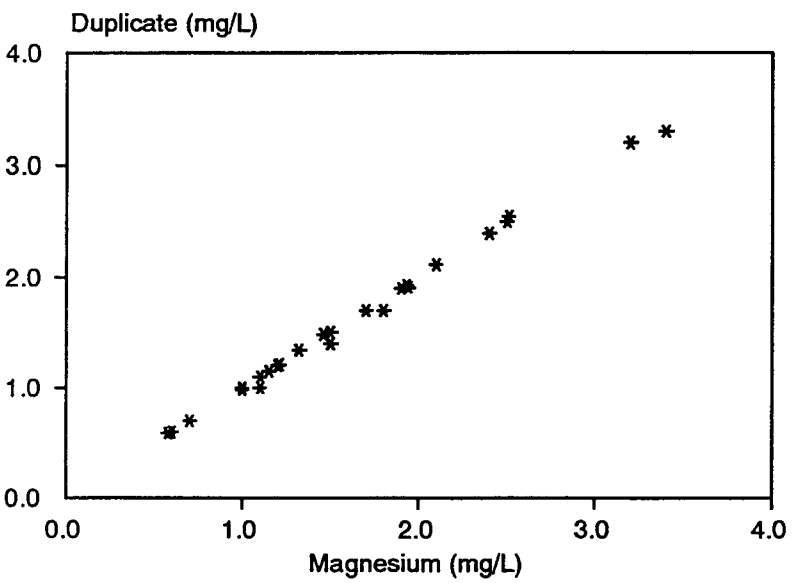


Figure A.2. A graphical and statistical summary of magnesium in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	4.68	4.71
Standard Deviation (mg/L)	0.58	0.56
Coefficient of Variation (%)	12.4	11.9
Difference of Means (%)	0.64	

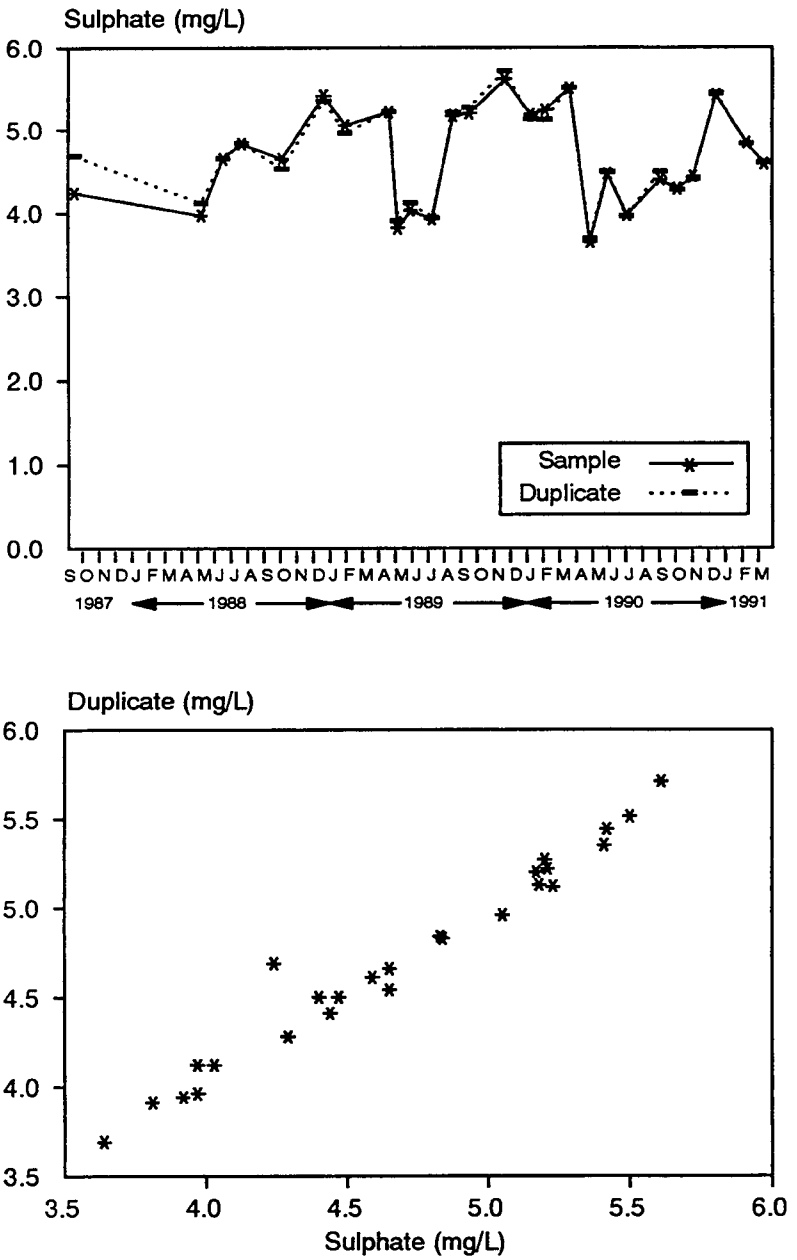
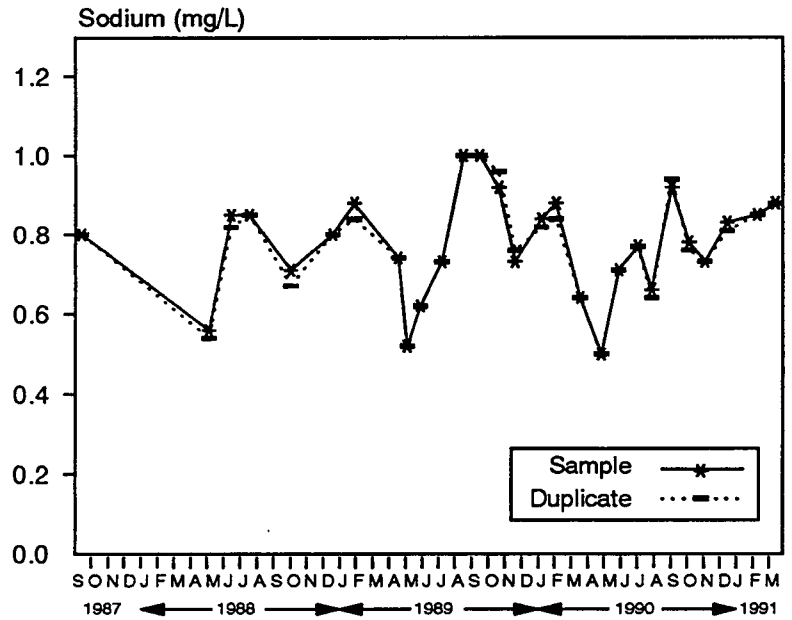


Figure A.3. A graphical and statistical summary of sulphate in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.78	0.77
Standard Deviation (mg/L)	0.13	0.13
Coefficient of Variation (%)	16.7	16.9
Difference of Means (%)	1.29	



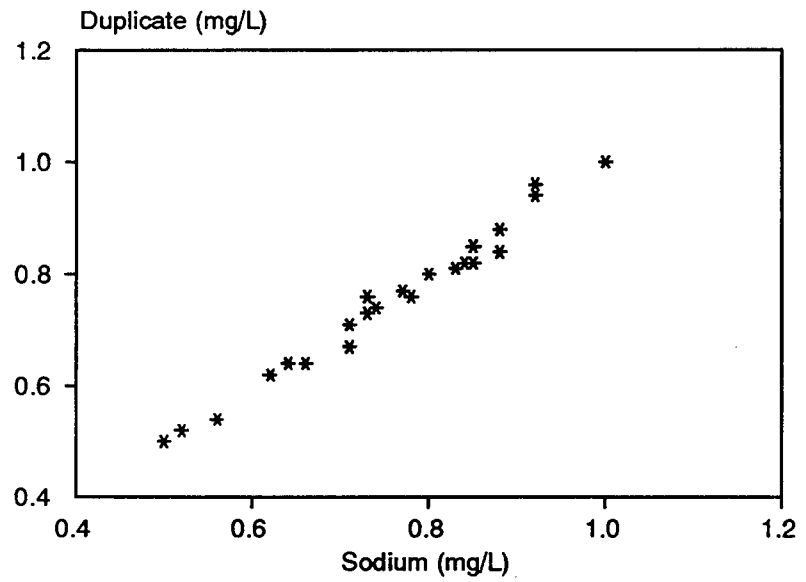


Figure A.4. A graphical and statistical summary of sodium in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.360	0.352
Standard Deviation (mg/L)	0.118	0.112
Coefficient of Variation (%)	32.8	31.8
Difference of Means (%)	2.25	

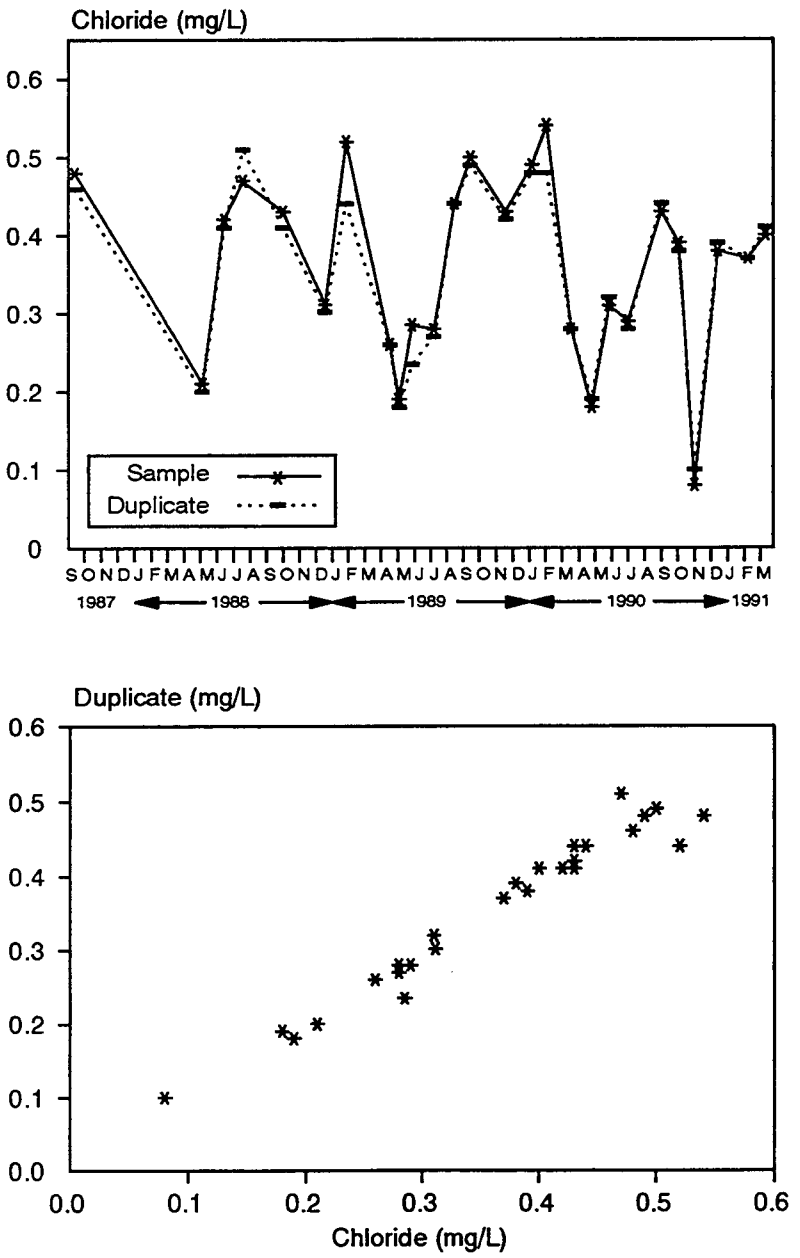


Figure A.5. A graphical and statistical summary of chloride in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.35	0.34
Standard Deviation (mg/L)	0.05	0.05
Coefficient of Variation (%)	14.3	14.7
Difference of Means (%)	2.90	

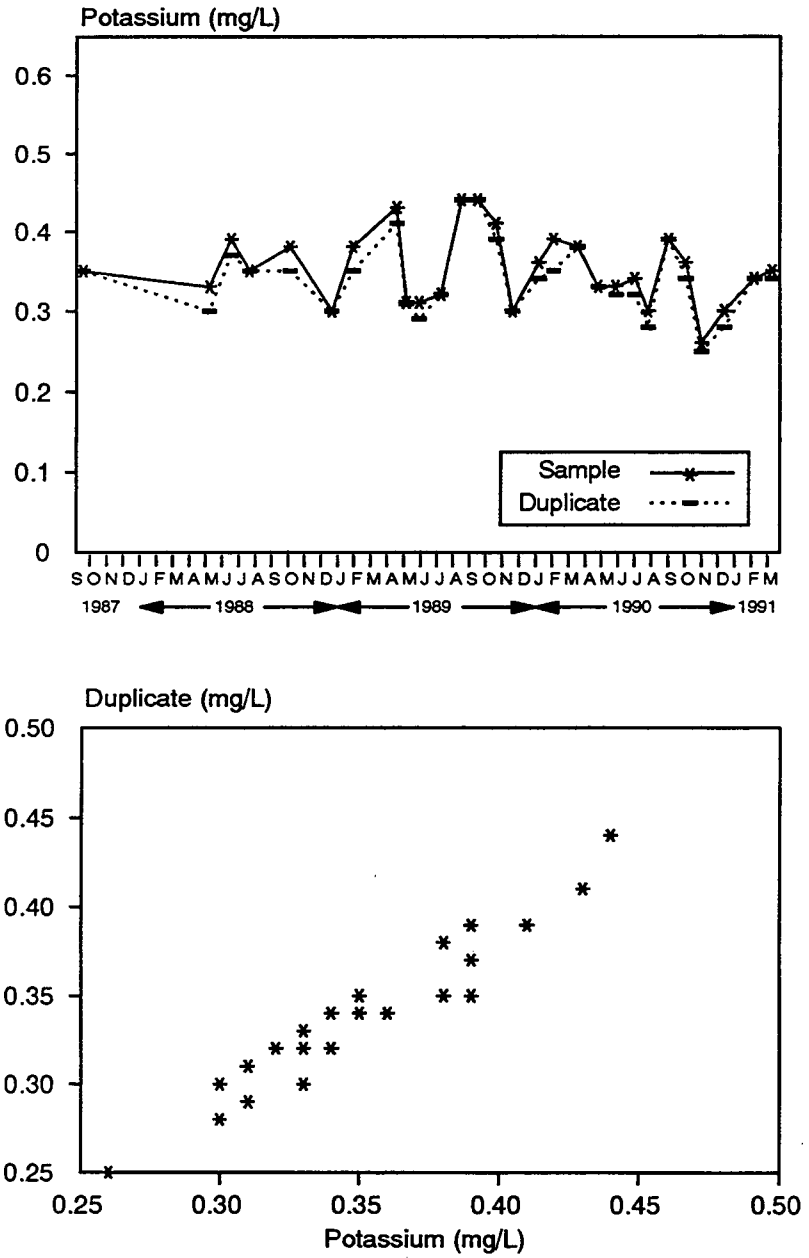


Figure A.6. A graphical and statistical summary of potassium in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.0804	0.0783
Standard Deviation (mg/L)	0.0378	0.0367
Coefficient of Variation (%)	47.0	46.9
Difference of Means (%)	2.65	

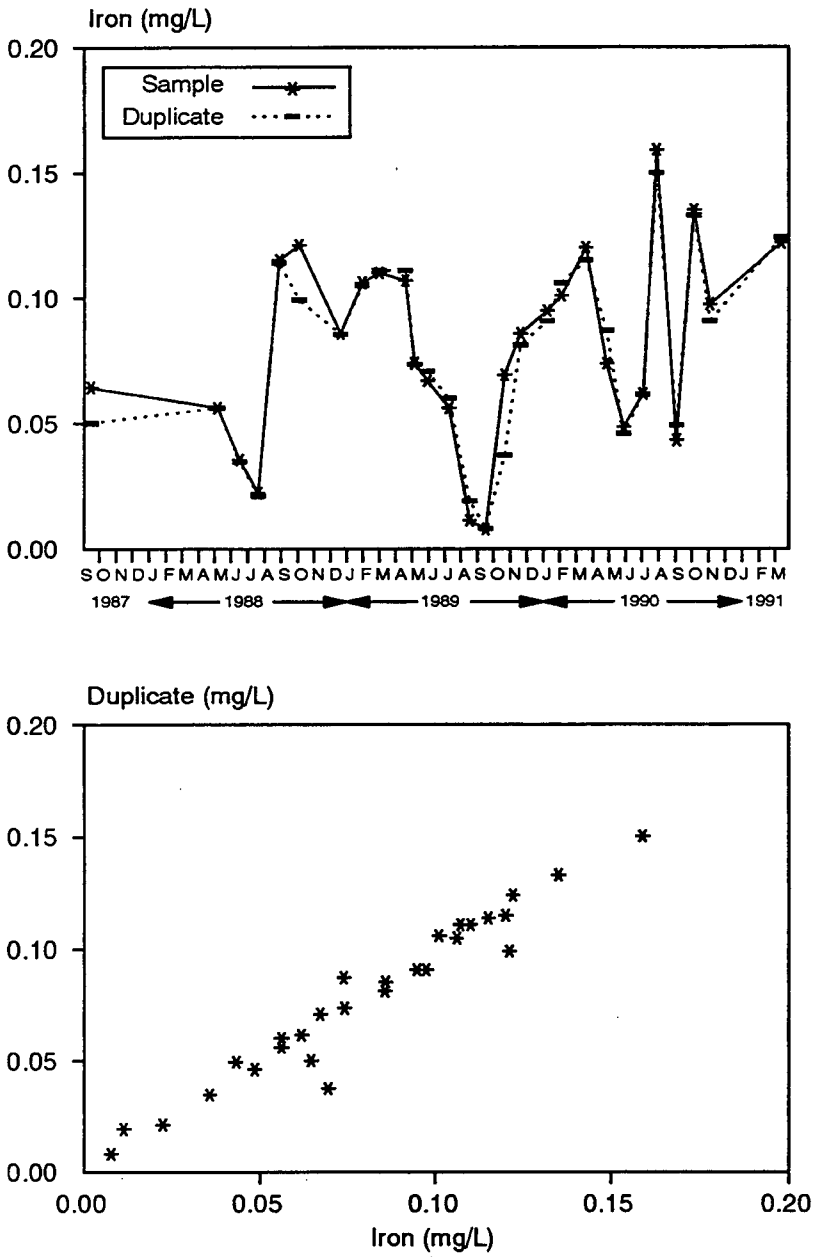
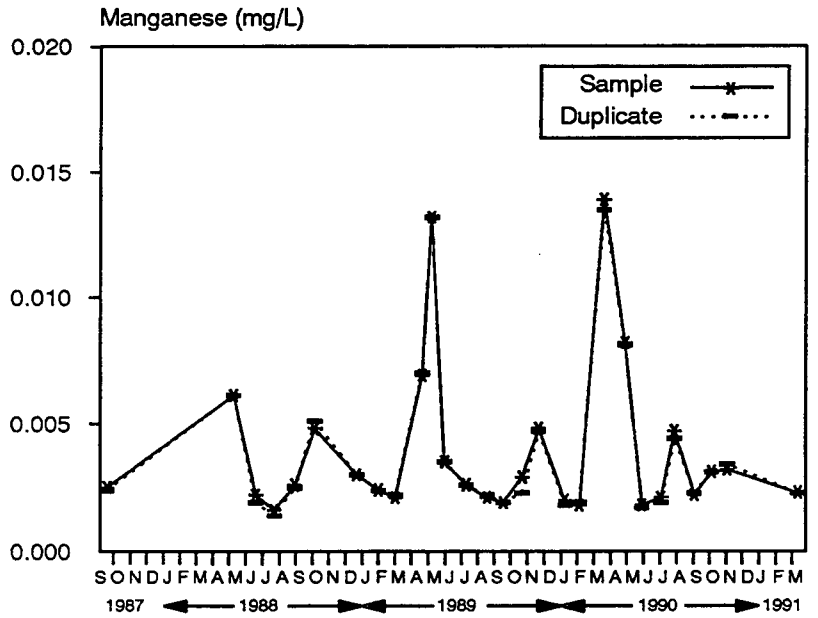


Figure A.7. A graphical and statistical summary of iron in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.0039	0.0039
Standard Deviation (mg/L)	0.0032	0.0032
Coefficient of Variation (%)	82.1	82.1
Difference of Means (%)	0	



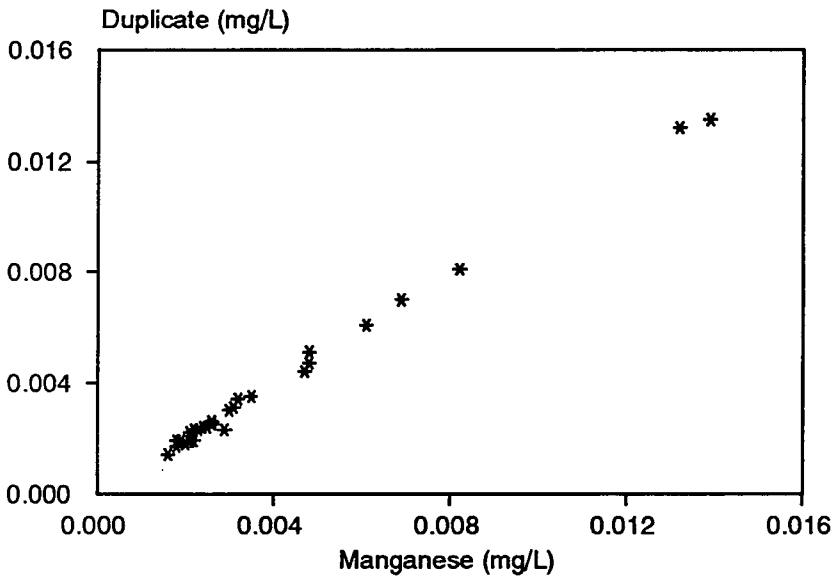
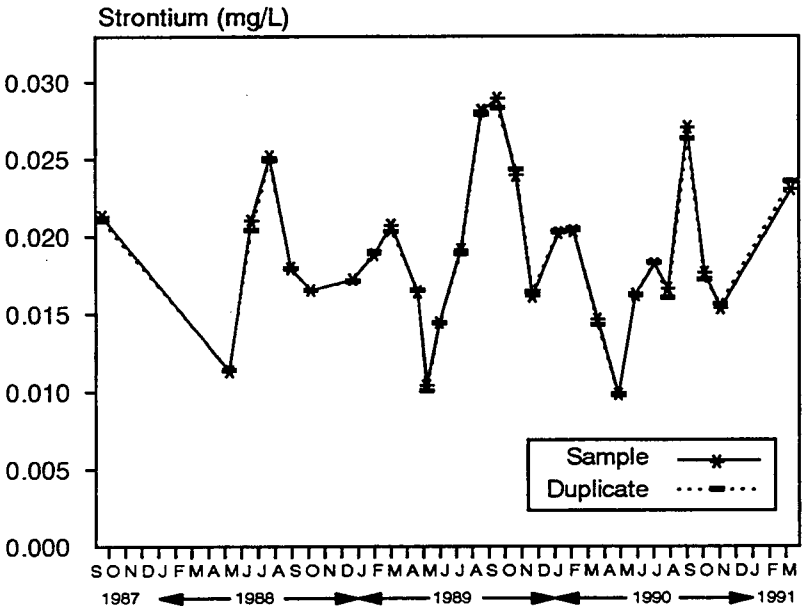


Figure A.8. A graphical and statistical summary of manganese in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.0188	0.0187
Standard Deviation (mg/L)	0.0049	0.0048
Coefficient of Variation (%)	26.1	25.7
Difference of Means (%)	0.53	



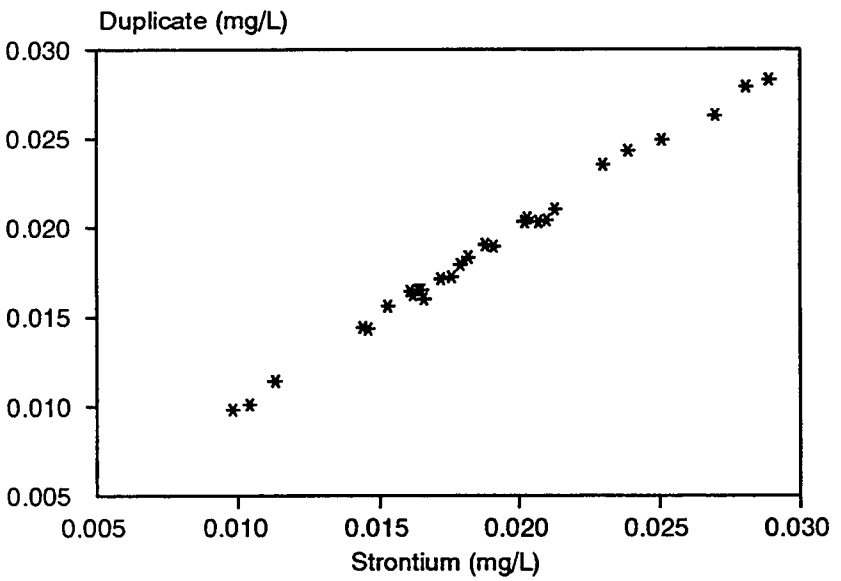
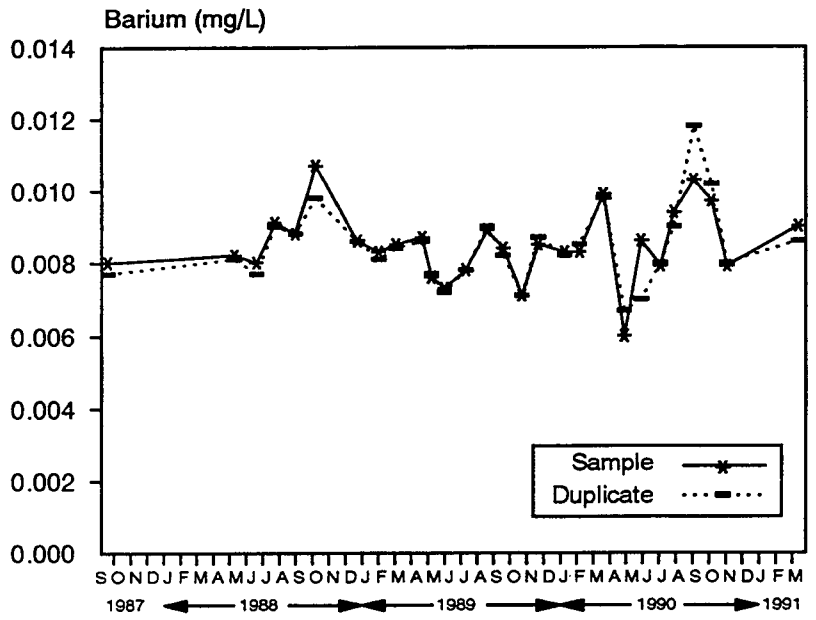


Figure A.9. A graphical and statistical summary of strontium in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

Statistical Profile	Sample	Duplicate
Mean (mg/L)	0.0085	0.0084
Standard Deviation (mg/L)	0.0010	0.0011
Coefficient of Variation (%)	11.8	13.1
Difference of Means (%)	1.18	



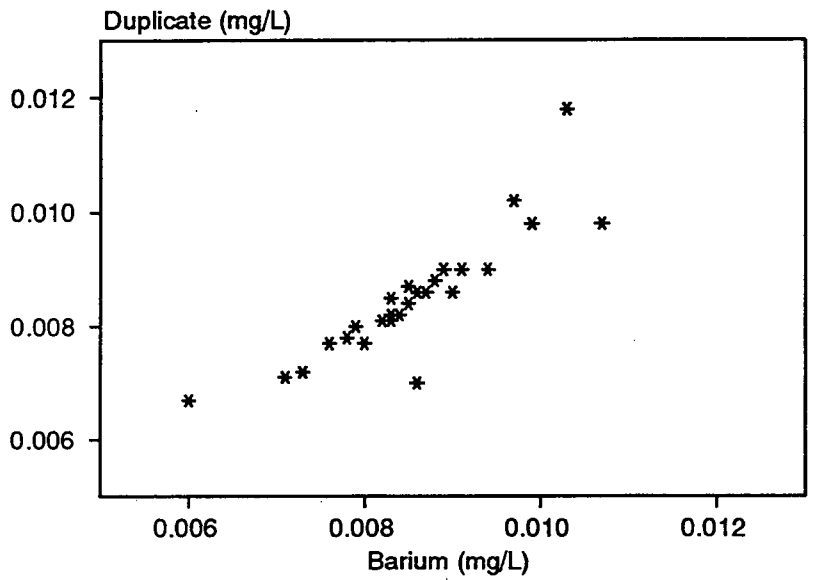


Figure A.10 A graphical and statistical summary of barium in duplicate filtered water samples collected from the (West) Pukaskwa River, September 1987 to March 1991.

CONTROLLING SAMPLE TEMPERATURES

Tom N. Webber

British Columbia

Ministry of Environment, Lands, and Parks

CONTROLLING SAMPLE TEMPERATURES

(Field to Lab Shipments)

Introduction:

-Federal Provincial Water Quality Monitoring Program currently operating 14 sites 12 months of the year from all over the province. Total number of sample sets = 395 routine samples & 44 for quality assurance samples.

-Working towards acquisition of consistent good data by eliminating as many factors as possible which are likely to corrupt analytical results.

-Can not rely on good statistics to fix bad data.

-Current use of 4° C as the limit for reduction/elimination of biological activity in samples (may not be applicable to northern regions).

Discussion:

1). Review current list of Zenon's Sample Container Preservation Criteria and compare with the 1993/94 Site, Variable & Shipping list used by the province.

2). Review **overhead** for record keeping and shipments received by Zenon; note temperature and transit time columns.

3). Review **overhead** for Check-list for Water Sampling and highlight items which relate to packing and cooling of samples in coolers.

4). Review **overhead** for Factors Affecting Sample Temperatures and Controlling Sample Temperatures. "Use a volume of ice about equal to sample volume during coolers months and double the volume in warmer months."

5). Review **overhead** for Marguerite and Creston sites to compare results of record keeping and sampler reliability in collecting, preserving and shipping of samples to the designated lab(s).

6). Review **overheads** (5 graphs) of Zenon's May, 1993 report on Sample Holding Times-A Study of Nutrient Depletion and/or Coversion. Note in particular comparisons between room temperature and 4° C for various temperature sensitive variables; ignore filtered vs unfiltered comparisons. "The study concurs with Zenon's standard operating procedures with regards to the treatment of samples prior to analysis. The 4° C (filtered) bottles show stability with every analyte with a slight exception with TDP, however, that was stable for two weeks."

Tom N. Webber
Biologist, Water Quality Branch
Victoria, B.C.
October 17, 1993

Factors Affecting Sample Temperatures

(From sample site to analytical Lab)

1). SHIPPING CONTAINER
   * Insulated ?
   * Size ?

2). VOLUME of SAMPLE WATER

3). TEMP. of SAMPLE WATER
   * Seasonal variation
   * Latitude and altitude etc.

4). AIR TEMPERATURE
   * During transit or storage.

5). NO. and SIZE of ICE PACKS

6). LOCATION of ICE PACKS
   * Contact with sensitive samples ?

7). TRANSIT TIME

8). SAMPLER RELIABILITY
   * Incentives ?

Controlling Sample Temperatures

(From sample site to analytical Lab)

1). SHIPPING CONTAINER

* sturdy & insulated
* just large enough to handle samples, preservatives & ice packs.

2). VOLUME of SAMPLE WATER

* minimum volume to complete analysis

3). TEMP. of SAMPLE WATER

* adjust sampling season
* pre-cool samples in freezer or fridge

4). AIR TEMPERATURE

* where is container during transit or storage ?

5). NO. and SIZE of ICE PACKS

* faster cooling with increased surface area
* longer cooling with more ice packs

6). LOCATION of ICE PACKS

* rearrange sensitive samples to contact ice packs.

7). TRANSIT TIME

* sample early in week, i.e., Tuesday or Wednesday
* re-evaluate transit mode & courier to speed delivery

8). SAMPLER RELIABILITY

* Hire reliable samplers, provide incentives for successful completions.

9). SENSITIVE VARIABLES

* re-evaluate need for sensitive variables

Zenon Environmental Laboratories

Sample Container and Preservation Criteria

1993

Water & Waste Water

BACTERIOLOGY:

Analysis Type:	Container Size:	Container, Type & Preparation:	Preservation:	Hold Times:
Coliform, E. Coli	250 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Coliform, Fecal	250 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Coliform, Total	250 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Enterococcus	250 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Fecal Streptococcus	250 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Salmonella	500 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Standard Plate Count	250 mL	Plastic, Sterilized	4°C, do not freeze	48 hours
Biomass	250 mL	Plastic	store frozen	N/A
BOD	1L	Plastic	4°C, exclude all air	48 hours
BOD & TSS	2L	Plastic	4°C, exclude all air	48 hours
Chlorophyll / Phaeophytin		Membrane or GF/C filter	store frozen in dark with dessicant	N/A
Microtox	100 mL	Amber Glass	4°C, exclude all air	5 days
Taxonomy, benthic Invertebrates	100 mL	Plastic Tissue Cup	70% ethanol or 10% Formalin, 4°C, dark	N/A
Taxonomy,periphyton	500 mL	Plastic	Lugols to tea colour, 3mL/L, 4°C, dark	N/A
Taxonomy, phytoplankton	1L	Plastic	Lugols to tea colour, 3mL/L, 4°C, dark	N/A
Taxonomy, zooplankton	1L	Plastic	70% ethanol, 4°C, in dark	N/A
Bioassay, Daphnia	4L	Plastic	4° C, exclude all air	5 days

INORGANIC ANALYSIS:

General Chemistry	4L	Plastic	keep cool, 4°C	72 hours
General Chemistry	2L	Plastic	keep cool, 4°C	72 hours
General Chemistry	1L	Plastic	keep cool, 4°C	72 hours
General Chemistry	500 mL	Plastic	keep cool, 4°C	72 hours
General Chemistry	250 mL	Plastic	keep cool, 4°C	72 hours
Carbon: TIC/TOC, Inorg/Org	100 mL	Plastic or Glass	4°C	72 hours
Phosphorus, Low level	100 or 250 mL	Amber Glass, Acid rinsed	keep cool, 4°C	72 hours

ORGANIC ANALYSIS:

Chlorophenols: PCP,TTCP, TCP	1L	Amber Glass, Solvent cleaned	4°C	30 days
Dioins & Furans	3 x 4L	Amber Glass, Solvent cleaned	4°C	30 days
EPA 624, Volatiles	3 x 40 mL	Glass vial, Baked, Solvent cleaned	4°C, Na2S2O3, Headspace-free	14 days
EPA 625, CP/OC/PAH/PCB	1L	Amber Glass, Solvent cleaned	4°C	30 days
Glyphosate	500 mL	Amber Glass, Solvent cleaned	4°C	30 days
Herbicides, Acid Extractable (AEH)	1L	Amber Glass, Solvent cleaned	4°C	30 days
Herbicides, Solvent Soluble	1L	Amber Glass, Solvent cleaned	4°C	30 days
Herbicides, Triazine	1L	Amber Glass, Solvent cleaned	4°C	30 days
Organochlorine (OC) pesticides	1L	Amber Glass, Solvent cleaned	4°C	30 days
Organophosphate (OP) pesticides	1L	Amber Glass, Solvent cleaned	4°C	30 days
Polycyclic Aromatic Hydrocarbons (PAH)	1L	Amber Glass, Solvent cleaned	4°C	30 days
Polychorinated Biphenyls (PCB)	1L	Amber Glass, Solvent cleaned	4°C	30 days
Petroleum Distillates (Hydrocarbons)	1L	Amber Glass, Solvent cleaned	4°C	30 days
PQ-8 (copper 8, copper quinolate)	250, 500 mL	Solvent cleaned glass, Foil lined cap	4°C, HCL to pH <2	30 days
Resin Acids	1L	Amber Glass, Solvent cleaned	4°C	21 days
TCMTB	1L	Amber Glass, Solvent cleaned	4°C	36 hours
THM's, Trhalomethanes	500 mL	Amber Glass, Solvent cleaned	4°C, Na2S2O3, Headspace-free	14 days
Volatiles / Gasoline / BTEX	500 mL	Amber Glass, Solvent cleaned	4°C	14 days
IPBC / DDAC	1L	Plastic	4°C, 6N HCL, 2mL/L	14 days

SOILS, SEDIMENTS,TISSUES and OTHERS:

Extractable Organic Halides (EOX)	50 g min	Solvent cleaned glass, Foil lined cap	freeze	6 months
Metals	100 g min	Wide mouth Plastic	keep cool, 4°C	6 months
Organic Carbon	100 g min	Plastic or Glass	keep cool, 4°C	6 months
Organics	100 g min	Wide mouth glass, Solvent cleaned	freeze	6 months
Particle Size Analysis	100 g min	Plastic or Glass	keep cool, 4°C	6 months
PQ-8 (copper 8, copper quinolate)	100 g min	Wide mouth amber glass, Solv. cleaned	freeze	6 months

F/P Ist temp sens var.

1993/94 FEDERAL-PROVINCIAL WATER QUALITY MONITORING AGREEMENT
SITE, VARIABLE & SHIPPING LIST

last update: March 8, 1994.

SITE NAME & SEAM NO:	SAMPLE FREQ.: per year Routine:	QA:	SAMPLE BOTTLE:	VARIABLES:
Fraser River at Hansard E206580	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Residue (Fil.)
				Ammonia (N. Diss.)
				P (Diss. Ortho)
				P (Total Diss.)
				Colour (TAC)
			250 mL Bacteriological	Fecal Coliform
Fraser River at Marguerite 0600011	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Residue (Fil.)
				Ammonia (N. Diss.)
				P (Diss. Ortho)
				P (Total Diss.)
				Colour (TAC)
			250 mL Bacteriological	Fecal Coliform
	22	3	**500 mL Organics**	AOX
Fraser River at Hope E206581	22	3		AOX
Nechako River at Prince George E206583	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Residue (Fil.)
				Ammonia (N. Diss.)
				P (Total Diss.)
			250 mL Bacteriological	Fecal Coliform
Thompson River at Spences Bridge E206586	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Residue (Fil.)
				Ammonia (N. Diss.)
				P (Total Diss.)
				DOP-Low Level
Peace River above Alces River E206585	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Ammonia (N. Diss.)
				P (Total Diss.)
			250 mL Bacteriological	Fecal Coliform
Columbia River at Revelstoke E206579	13	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Ammonia (N. Diss.)
				P (Diss. Ortho)

Sample bottles in BOLD contain temperature sensitive variables & must be returned to the Lab at less than or equal to 4° C.

SITE NAME & SEAM NO:	SAMPLE FREQ.: per year Routine:	QA:	SAMPLE BOTTLE:	VARIABLES:
Columbia River at Birchbank 0200003	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Ammonia (N. Diss.)
				P (Diss. Ortho)
				P (Total Diss.)
				Colour (SWL)
				Colour (TAC)
			250 mL Bacteriological	Fecal Coliform
Columbia River at Waneta 0200559	52	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Ammonia (N. Diss.)
				P (Diss. Ortho)
				P (Total Diss.)
				Colour (SWL)
				Colour (TAC)
			250 mL Bacteriological	Fecal Coliform
Kootenay River at Fenwick Station 0200038	26	3	**2 L General**	Residue (non-fil.)
				Ammonia (N. Diss.)
				P (Diss. Ortho)
				Colour (SWL)
Kootenay River at Creston E206587	26	3	**2 L General**	Residue (non-fil.)
				Ammonia (N. Diss.)
				N (total KJELDAHL)
				N (Total Organic)
			125mL Low Level	P (DOP-low level)
			250 mL Bacteriological	Fecal Coliform
Elk River at Highway 93 Bridge 0200016	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Ammonia (N. Diss.)
				P (Diss. Ortho)
Okanagan River at Oliver 0500720	26	3	**1 L NFR**	Residue (non-fil.)
			2 L General	Ammonia (N. Diss.)
				P (Diss. Ortho)
				P (Total Diss.)
			250 mL Bacteriological	Fecal Coliform
Salmon River at Highway #1 Bridge E206092	26	2	**1 L NFR**	Residue (non-fil.)
			2 L General	Residue (Fil.)
				Ammonia (N. Diss.)
				P (Diss. Ortho)
				P (Total Diss.)
				N (total KJELDAHL)
				N (Total Organic)
			250 mL Bacteriological	Fecal Coliform
Total # Samples per Year:	**395**	**44**		

Federal/Provincial Water Quality Monitoring Program

1993/94

Inspection Date:
Inspected By:
Page of:

Samples received for the Week ending:

SITE: (SEAM No.)	REQUISITION No.:	SAMPLING DATE: (YY MM DD)	RECEIVED DATE: (YY MM DD)	LAB TECH: (Initial)	*SAMPLE INFO:* Temp. (°C)	Type: *	Transit: (days)	*COMMENTS:* (missing samples, long transit time, warm sample temp. etc.)

* R = routine; FB = field blank; LB = lab blank; FR = field replicate.

T. Webber 07/12/93

FEDERAL-PROVINCIAL WATER QUALITY MONITORING PROGRAM

Check-list for Water Sampling

Date: _____

Site: _____

Sampler _____

Observer: _____

last update: October 21, 1993

T. Webber

STEP or PROCEDURE:	OKAY ?	COMMENTS:
sampling day and shipping arrangements carefully planned to minimize transit delays.		
bottles clearly labelled & dated before wetting, i.e., uses a permanent marking pen.		
sampler & rope are clean before use.		
bottle caps removed just before sampling, are protected from contamination i.e., placed in a clean, dry plastic bag; avoids touching inside of caps and bottles.		
exercises caution when sampling; generally safety conscious around site.		
sample taken at designated sampling site; any deviations from site location recorded.		
samples in deep, well-mixed & flowing water whenever possible.		
samples upstream when wading; avoids collecting in stirred-up water.		
avoids causing debris from falling from bridge onto the sampler.		
sample bottles are not rinsed before collection (i.e., are lab pre-cleaned).		
bottles filled to correct level & securely capped immediately after filling. i.e., room for preservatives, small air space for coliforms.		
handles preservatives carefully with appropriate safety equipment, i.e., gloves & glasses; demonstrates technique that minimizes preservative contamination; empty preservative vial re-capped, placed inside secondary container and returned to cooler.		
no contact between preservative vial or dispenser & sample water or sample bottle.		
no contact with sample water, inside of bottles or caps with anything !		
allowed thermometer to equilibrate 3 to 4 minutes in "field" bottle before reading; thermometer never inserted in any sample bottle.		
sampling time recorded as hh/mm (2400 hour clock); sample date as yy/mm/dd on all lab requisitions.		
packs bottles carefully with enough ice packs to cool temperature sensitive samples.		
records field measurements, observations & possible contamination sources where appropriate.		
reuseable sampling & safety equipment is kept clean & stored for future use in such a manner as to minimize damage or contamination.		
shipping coolers secured (taped) for transit; destination clearly labelled on cooler(s).		

Controlling Sample Temperatures
(From sample site to analytical Lab)

1). **SHIPPING CONTAINER**

* sturdy & insulated
* just large enough to handle samples, preservatives & ice packs.

2). **VOLUME of SAMPLE WATER**

* minimum vol. to complete analysis

3). **TEMP. of SAMPLE WATER**

* adjust sampling season
* pre-cool samples in freezer or fridge

4). **AIR TEMPERATURE**

* where is container during transit or storage ?

5). **NO. and SIZE of ICE PACKS**

* faster cooling with increased surface area.
* longer cooling with more ice packs

6). **LOCATION of ICE PACKS**

* rearrange sensitive samples to contact ice packs.

7). **TRANSIT TIME**

* sample early in week, i.e., Tuesday or Wednesday
* re-evaluate transit mode & courier

8). **SAMPLER RELIABILITY**

* Hire reliable samplers, provide incentives for successful completions.

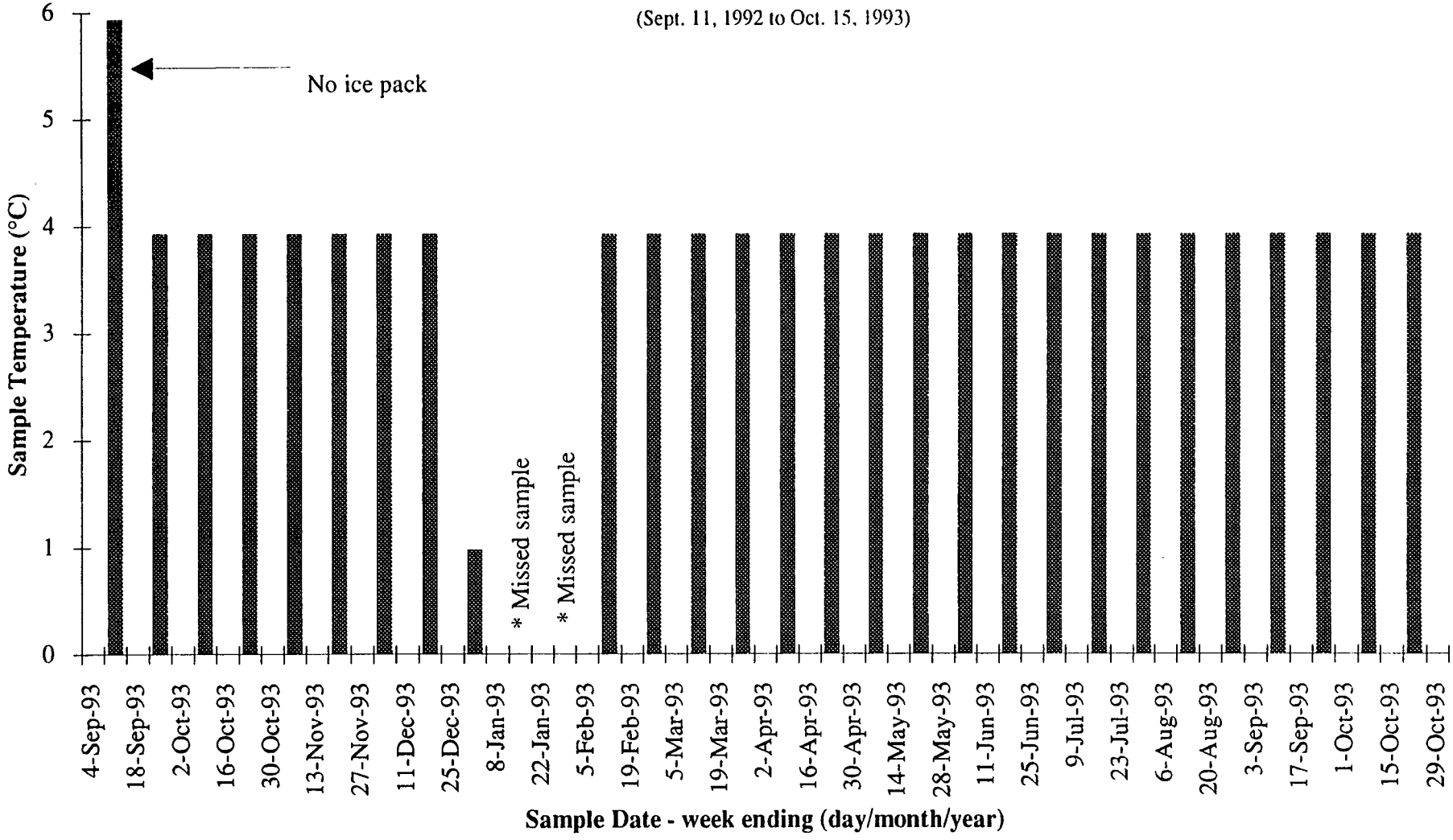
9). **SENSITIVE VARIABLES**

* re-evaluate need for sensitive variables

Kootenay River at Creston

Water Sample Temperatures

(Sept. 11, 1992 to Oct. 15, 1993)



* = missed sample due to weather & ice conditions.

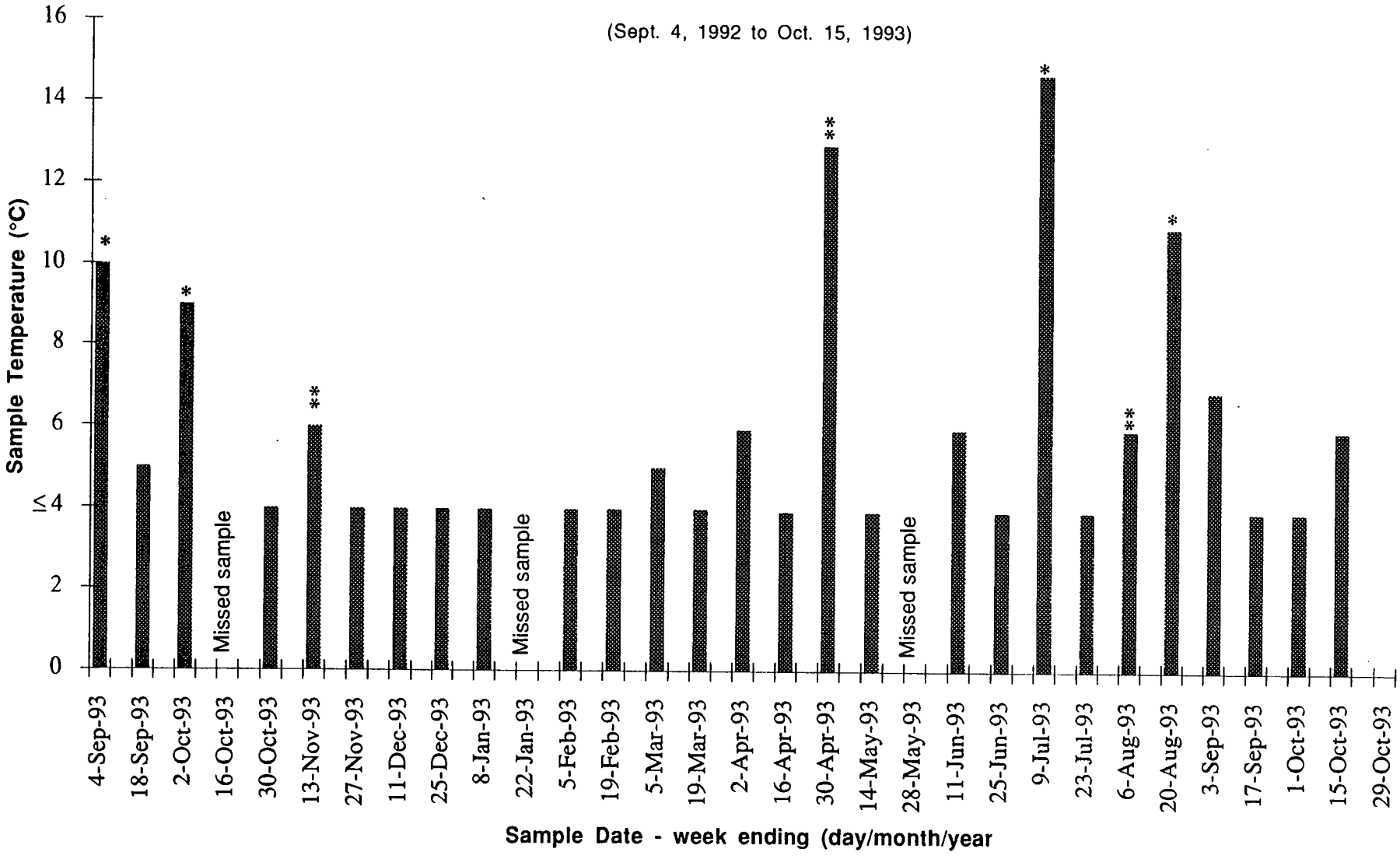
Transit time = 48 hours or less.

Sample temperatures are recorded as less than or equal to 4° C

Fraser River at Marguerite

Water sample Temperatures

(Sept. 4, 1992 to Oct. 15, 1993)



* = empty, missing or non-frozen ice pack

** = transit time to lab longer than 48 hours.

Sample Holding Times - A Study of Nutrient Depletion and/or Conversion

Prepared For: Steve Horvath
BC Ministry of Environment

Prepared By: Robert Gilbert

Analysts: Brad Henderson
Lauretta Liem
Robert Gilbert

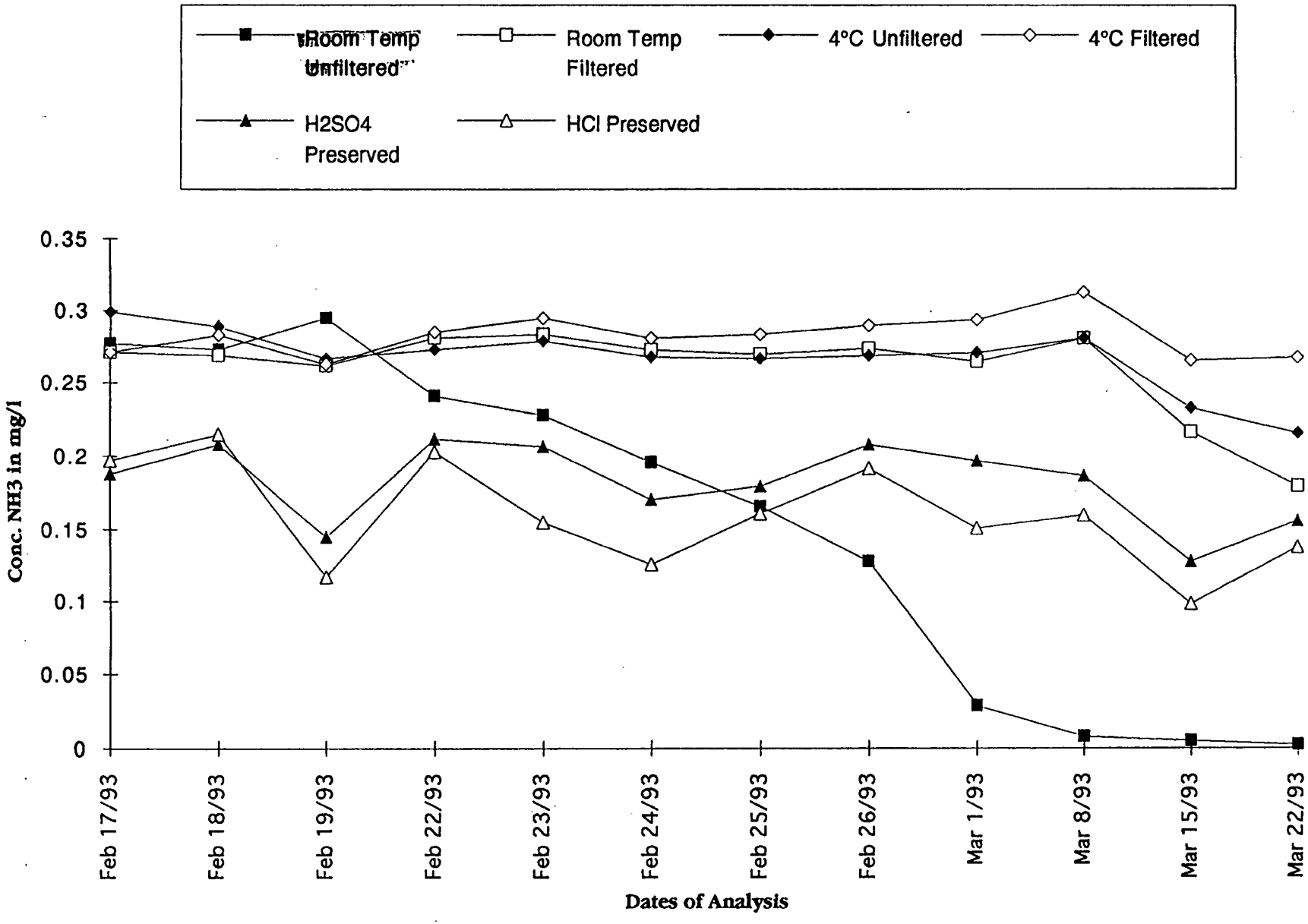
Statistical Analysts: Dr. Dorothy Jeffery

Zenon Environmental Laboratories Inc. (BC)
8577 Commerce Court, Burnaby, B.C., V5A 4N5

May 1993

Graph VII

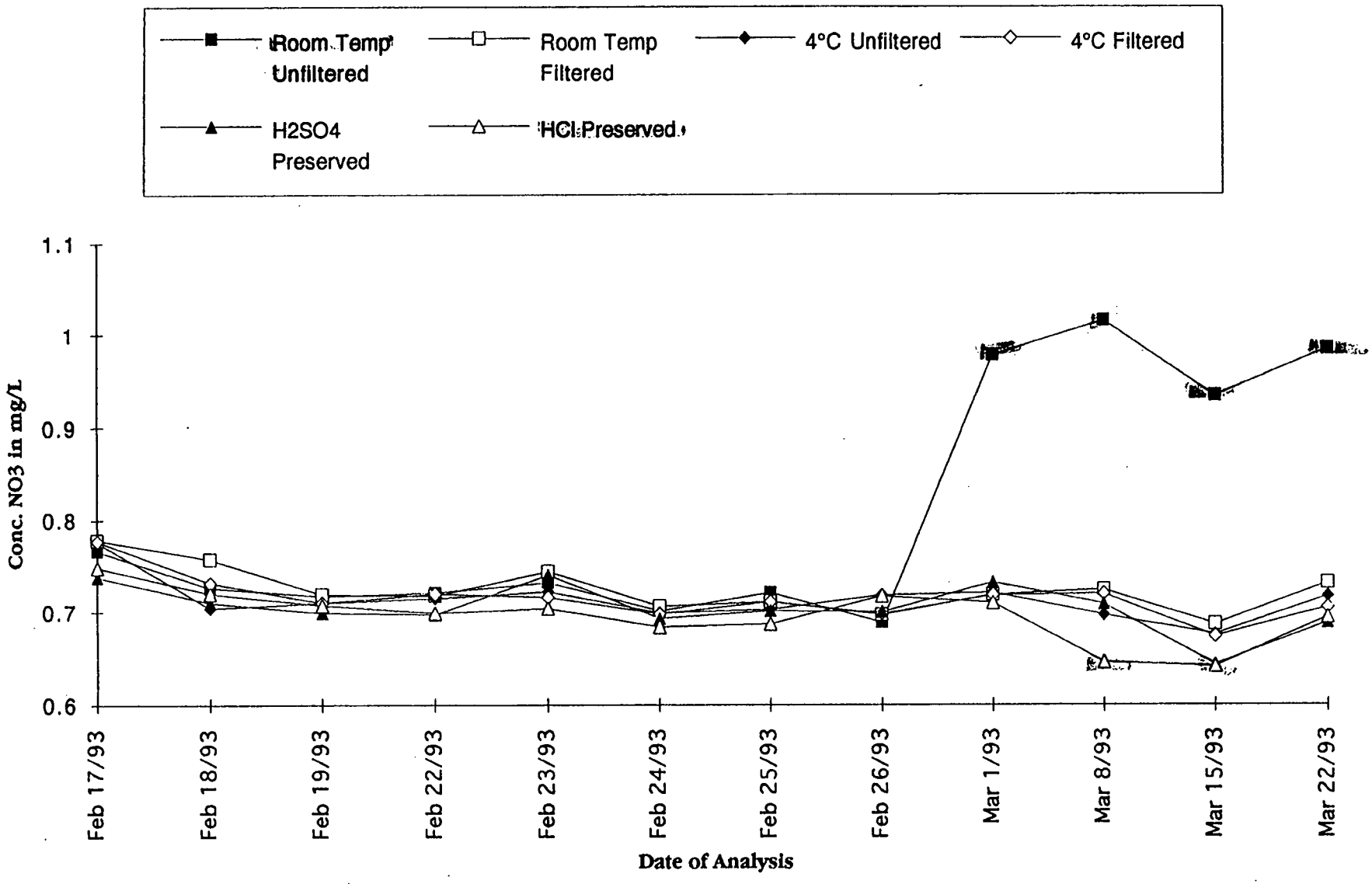
Site #4 - Ammonia (as N)



Nutrient Depletion Study - May 19,1993

Graph VIII

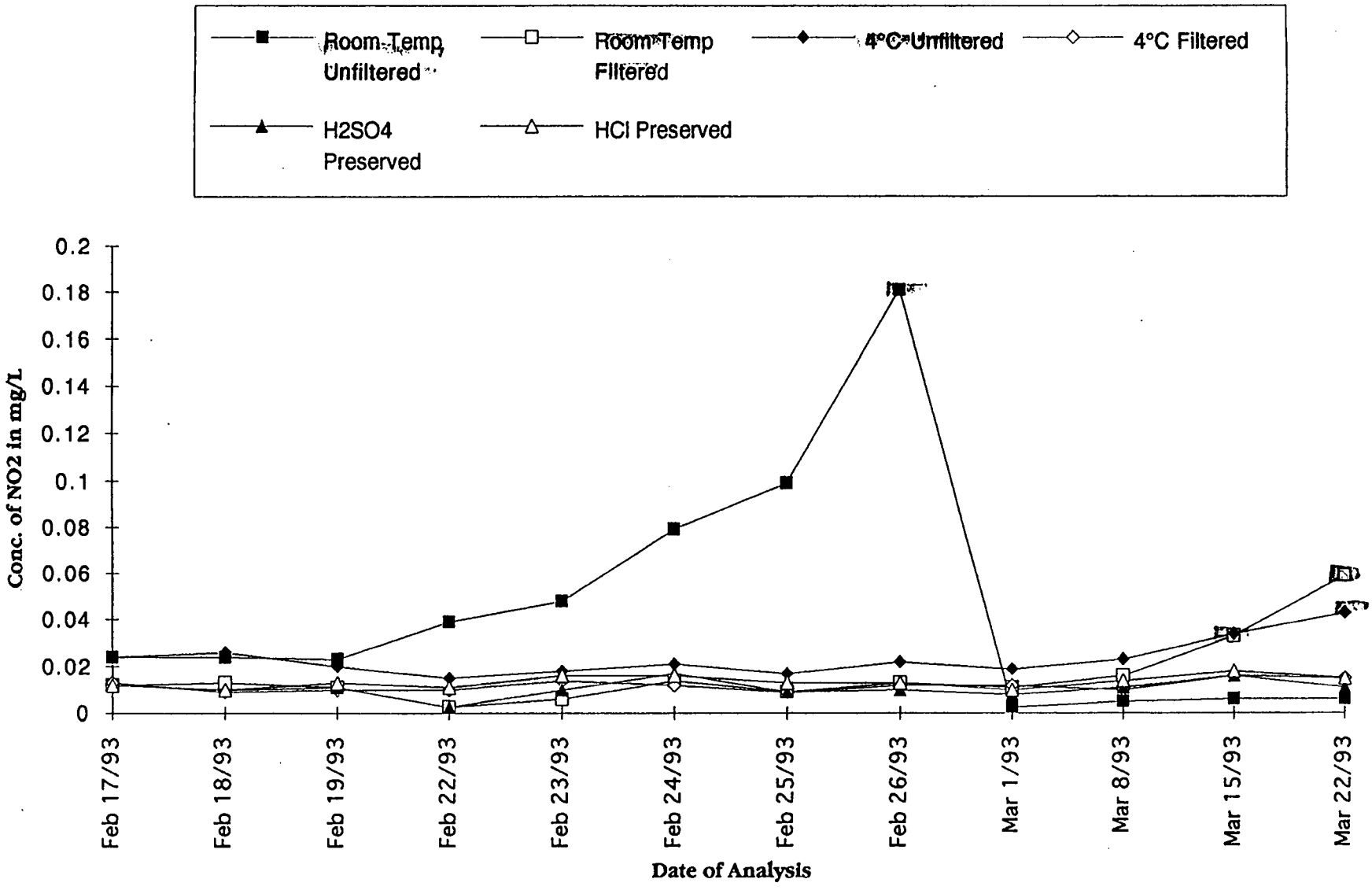
Site #4 - Nitrate (as N)



Nutrient Depletion Study - May 19, 1993

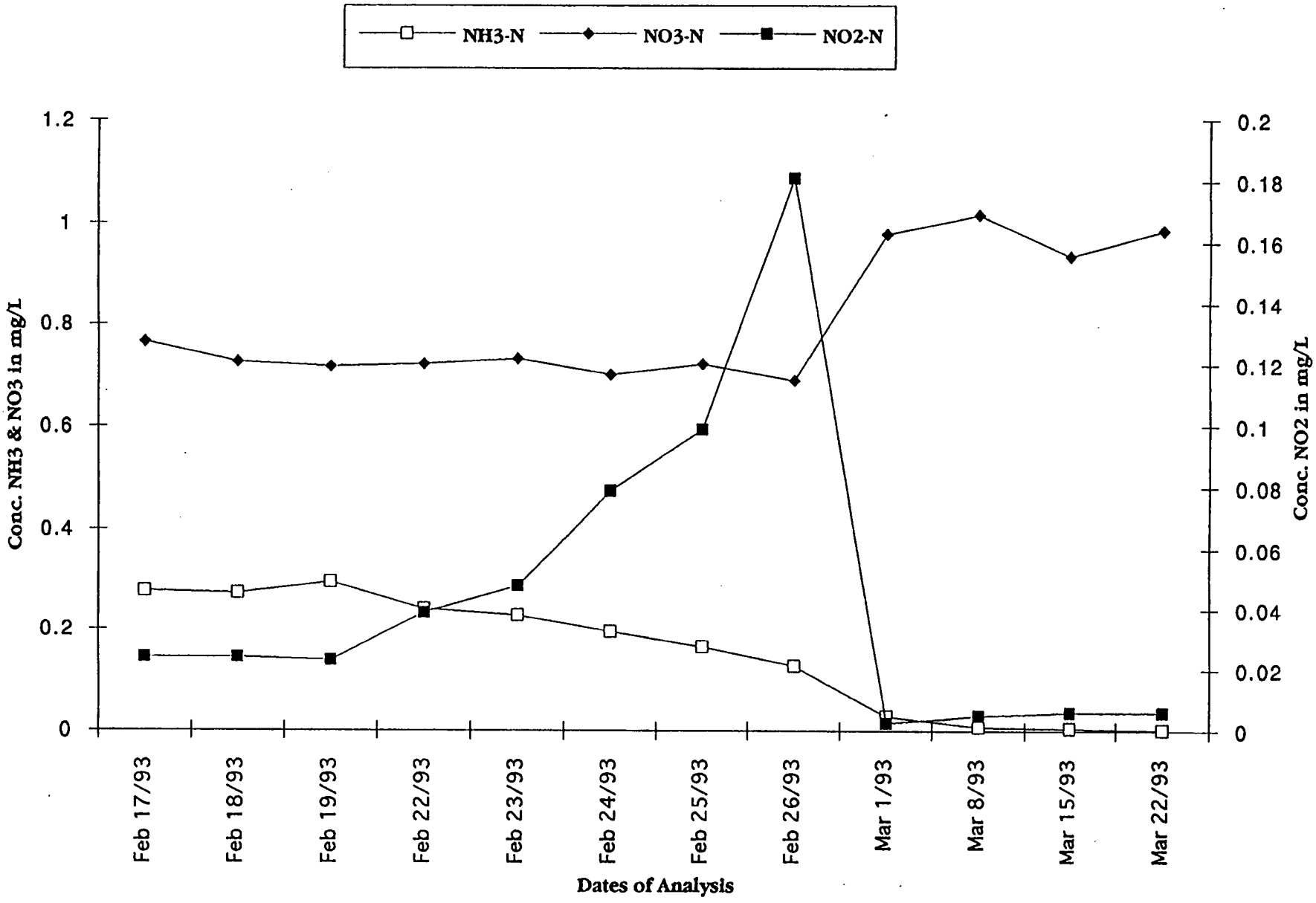
Graph IX

Site #4 - Nitrite (as N)



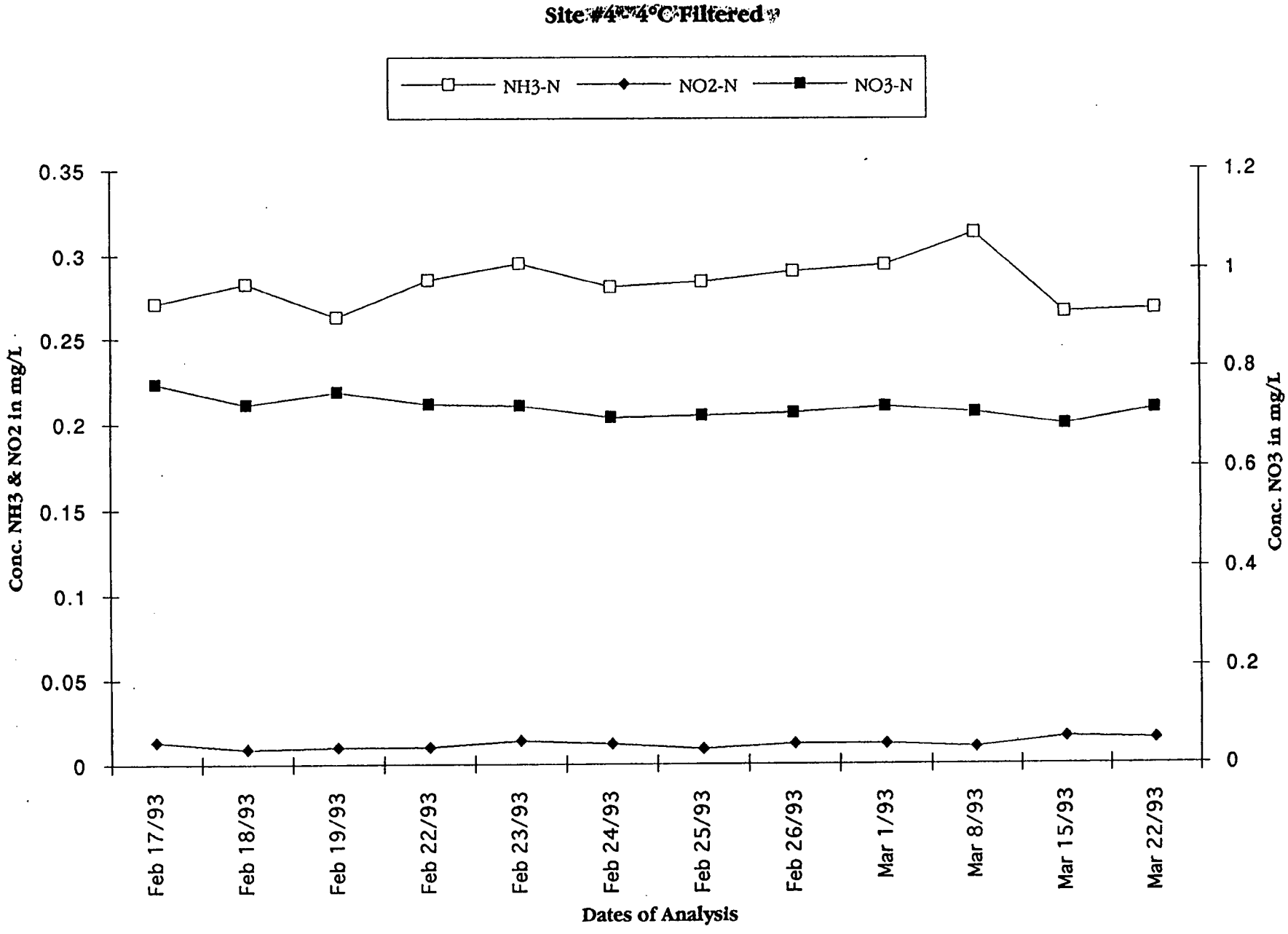
Nutrient Depletion Study - May 19, 1993

Site #4 - Room Temperature Unfiltered



Nutrient Depletion Study - May 19,1993

Graph XI



Nutrient Depletion Study - May 19,1993

pH MEASUREMENTS

Colin J. P. McKean

British Columbia

Ministry of Environment, Lands, and Parks

MINISTRY OF ENVIRONMENT
PROVINCE OF BRITISH COLUMBIA

pH DETERMINATION AND MEASUREMENT

Colin J.P. McKean
Brent W. Huggins
Resource Quality Section
Water Management Branch

November 1989

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1. INTRODUCTION

pH is a measure of the hydrogen ion activity not concentration. The modern pH electrodes develop an electromotive force (emf) that is proportional to the H^+ activity. The emf from the glass electrode is compared to the constant emf developed by the liquid junction potential of the reference electrode. The pH measurement is essentially a determination of an emf between the glass and reference electrodes (potentiometric measurement). Inaccurate pH measurements occur when the emf of the glass electrode is not properly calibrated with buffer solutions, or there are fluctuations in the constant potential developed by the reference electrode.

The purpose of this report is to outline the function, calibration, and storage of the glass and reference pH electrodes inorder to reduce problems and errors with pH measurements. Dole (1941) noted that if we wish to compare pH results with those obtained by other workers, we must standardize methodologies, because comparison of numbers based on different standards and conditions are meaningless.

2. DEFINITIONS

2.1 pH

pH is a measure of the hydrogen ion activity (aH^+) of a solution and is defined by the equation $pH = -\log aH^+$.

2.2 CONDUCTIVITY

The electrolytic conductivity of a water body refers to its ability to carry an electric current, which in turn is related to the total concentration of ions (i.e., charged solutes). This relationship depends on the geometry of the electrodes (area and distance apart), the temperature and, to some extent, on the nature of the major ions in solution. A pH electrode is actually a type of conductivity probe which is sensitive to hydrogen ions.

2.3 ACIDITY

Acidity of water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end-point pH used in the determination. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminum sulphates may contribute to the measured acidity according to the method of determination (Figure 1).

2.4 ALKALINITY

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used (pH 4.5 or inflection point; Figure 1). Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is

known (anion/cation balance). For specific discussion on the measurement of alkalinity see McQuaker et al., (1983) and McQuaker (1976).

Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents (Figure 1). The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present.

Very acidic (pH<4.5) or alkaline (pH>10) waters have appreciably higher conductivities than that expected from total ionic concentration, because of the high molar conductivities of H^+ or OH^- ions. In waters of high conductivity (>1000 $\mu S\ cm^{-1}$), including brackish waters, the molar conductivity and H^+ activity are appreciably reduced because of suppression of ionization (ionic inactivation).

When designing a new sampling program on a water system of unknown attributes, determining (or measuring) the anion/cation balance of the conservative elements (sodium, calcium, magnesium, chloride, bicarbonate and sulphate) is recommended. The ion pairs for the water sample can be reconstructed using the procedures by Riehl (1971) (Appendix 1). Because these elements are conservative in nature, a sample taken in winter and summer every 5 years is adequate.

2.5 BUFFERS

A buffer is a weak acid or base which can oppose changes in H^+ concentration by binding or releasing H^+ to resist change in pH. If 10^{-3} moles of a strong acid are added to a litre of water, it dissociates completely changing the H^+ concentration from 10^{-7} to 10^{-3} (pH 7 to 3). If 10^{-2} M of a weak acid is present and half dissociates to A^-* at pH 7, then

---

*A = conjugate base of weak acid $HA \geq H^+ + A^-$

the addition of the 10^{-3} moles of strong acid will result in nearly 10^{-3} moles of A^- being converted to HA. A negligible proportion (1 in 50,000) of the 10^{-3} moles of H^+ added will add to the concentration of free H^+. The latter will change from 1.0×10^{-7} to 1.5×10^{-7} M (pH 7.0 to 6.8). This act of resisting pH change is called buffering.

3. BUFFERS

3.1 NORMAL BUFFERS

1) Use commercial buffer reagents outlined in Table 1. Note the pH of the buffer solutions changes with temperature.

2) In situations where the conditions governing the formation of calcium carbonate (marl) are being studied, a standard solution in equilibrium with calcium carbonate is recommended. Using the formula below, the pH of distilled water in equilibrium with $CaCO_3$ (calcite) is 8.34, assuming the partial pressure of $CO_{2(g)}$ is one atmosphere and the temperature is 25 °C.

$$H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-} \qquad \log K^\circ = {}^-16.69$$

At pH 8.34 the above reaction will be in equilibrium with atmospheric CO_2 and calcite.

3.2 LOW IONIC STRENGTH BUFFERS

Low ionic* strength buffers are available for solutions below pH 5; however, low ionic strength buffers for pH 7 have not been developed. The recommended calibration procedure for low ionic strength waters is to use normal pH 7 buffer and a low ionic strength pH 4 buffer. Sandberg (pers. comm.) observed a significant difference in pH between the recommended procedure and the use of normal ionic buffers. The low ionic strength buffers can be purchased from Canlab or prepared using the following procedure:

---

* low ionic strength freshwater has a specific conductivity of ≤ 200 µS/cm.

1. Purchase 0.1 N sulphuric acid* and complete 3 serial dilutions to obtain 0.0001 N H_2SO_4 (one serial dilution = 10 mL of acid per 100 mL of distilled water). Use boiled distilled water to eliminate $CO_{2(g)}$ and carbonic acid from solution.

2. Place the pH 4 buffer thus prepared in a sealed container to avoid CO_2 contamination.

---

* use assured quality or equivalent acids

4. pH MEASUREMENT

pH may be estimated with coloured indicators (e.g., multi-range pH papers (not recommended for accurate measurements) or Taylor Comparitors etc.), but is measured more accurately with a pH meter, a reference electrode, and a glass electrode. A combination pH electrode consists of a reference and a glass electrode contained in a single unit (Figure 2).

4.1 REFERENCE ELECTRODE

The reference electrode typically has a calomel ($Hg/HgCl_2$) or a silver-silver chloride wire immersed in 3 M or saturated KCl. The reference electrode is in contact with the external solution (sample) by means of a porous ceramic disc, fritted glass, or semipermeable membrane. Diffusion of the reference electrolyte into the sample creats a liquid junction potential, which is relayed to the pH meter by the calomel or silver-silver chlorine lead out. The liquid junction potential is stable and constant in most freshwater environments, however, it can be unstable in very dilute waters ($\leq$ 50 μS/cm).

Most reference electrodes use a 3 M KCl electrolyte saturated with AgCl. Without the saturation of AgCl, the KCl would gradually dissolve the silver chloride layer on the lead-out, causing the response of the electrode to become unstable. Lead-outs used in conjunction with AgCl-free KCl solutions contain sufficient amounts of AgCl within the element to saturate the area around it and eliminate corrosion (e.g., Argenthal electrodes, Ingold Industries Ltd). Check the manufacturers specifications before preparing or purchasing KCl electrolyte.

Silver chloride can precipitate around the liquid junction if the reference electrolyte evaportates, or the molarity of the reference electrolyte increases. Silver sulphide can also precipitate around the liquid junction if the probe is exposed to sulphides. These precipitates contaminate the liquid junction and alter its potential causing zero-point drift and errors in the determination of pH.

A new type of reference electrode has been developed which uses a solid pressure resistant gel material that is saturated with KCl. An aperture exposes the gel to the sample solution, allowing the diffusion of electrolyte, and the formation of a liquid junction potential. One advantage of the gel filled reference electrodes is they do not require a Ag/AgCl lead-out, and AgCl is not required in the electrolyte. Consequently, contamination of the aperture is avoided.

Unlike normal reference electrodes, gel-filled electrodes show definite ageing phenomena because:

1. KCl diffuses continually from the gel into the sample solution. Reduction in electrolyte concentration causes zero-point drift, lower liquid junction potentials, and larger measuring errors.

2. Infiltrated sample solutions cannot be removed easily from the gel.

The storage of gel-filled reference electrode requires special treatment (see Section 5.2).

4.2 GLASS ELECTRODE

In recent years, the glass electrode has tended to replace all other types of pH indicators. The platinum/hydrogen gas electrode is only used for thermodynamic investigations or for the very accurate pH determination.

The glass electrode has the same lead-out (calomel or silver-silver chloride) as the reference electrode. The lead-out extends into a glass reservoir containing a buffered solution with a constant hydrogen ion activity. The glass of the reservoir is made of special glass which is selectively sensitive to H^+ ions. A difference in the hydrogen ion activity between the external solution and the internal buffer solution creates a electronic potential (called the boundary potential) which can be measured with respect to the liquid junction potential of the reference electrode. The boundary potential is proportional to the hydrogen ion activity of the sample solution. A sensitive high-impedance millivolt meter is used to measure the boundary potential.

The potential (E) generated by the glass electrode can be calculated theoretically using Nernst's equation:

$$E = E^\circ + E_N(\log aH^+)$$

where E° = a constant characteristic of the probe, E_N is known as Nernst's potential, and its value is influenced by temperature.

0°C	E_N = 54.2 mV
20°C	E_N = 58.2 mV
25°C	E_N = 59.2 mV
50°C	E_N = 64.1 mV

The measurable electrode-assembly potential E is the result of several components, as shown in Figure 3. E_1 (the boundary potential) is the only potential which is of interest in the pH measurement. All the other individual potentials E_2-E_6, are constant (assuming the probe is working properly), and are included in the standard potential E°. Since these individual potential components are all subject to a certain error, there is a dispersion of E° as a probe ages, and from one probe to another. This is why slope calibration is necessary.

The slope (change in emf potential per pH unit) is a very important parameter of any pH electrode. New electrodes should have a slope exceeding 98% of the theoretical value E_N. Since the slope varies slightly from electrode to electrode, slope calibration is recommended for accurate pH measurements. Some pH meters have a mV setting which can be used to directly calculate the electrode response per unit pH. The Hydrolab multiprobe sensor does not have a mV setting. For these units the glass electrode requires replacing when the slope calibration cannot lower the read out of a pH 4 buffer solution by 0.2 pH units, or raise the read out of a pH 9 buffer above 9.2.

The ablility of certain types of glass separating solutions of different hydrogen ion activities to develop a boundary potential was first demonstrated by Cremer in 1906 (Bates, 1973). Since that time, the formulation of the glass has been steadily improved, so that modern pH electrodes approach the accuracy of a platinum/hydrogen electrode. Studies of glasses by means of X-ray diffraction reveal a network of oxygen atoms (Figure 4), held together in irregular chains by silicon atoms (Bates, 1973). Each silicon atom is presumably associated with four oxygen atoms, and each oxygen atom is shared by two SiO_4 groups, to form a three-dimensional network. The oxygen atoms are relatively large (about 1.4 A in diameter as compared with 0.4 A for silicon), and hence make up the

bulk of the network. The holes in the three dimensional pattern are occupied by cations, held in place by the electrostatic fields of the neighboring oxygen ions. However, as a result of the irregularity of the silicon-oxygen lattice, the cations occupying the holes in the lattice possess many different energy levels. In other words, the work required to remove a cation from the lattice may be different for each individual ion. The ability of a group of negative ions to retain positive ions within the glass, determines the "anionic field strength".

The glass of a glass electrode contains roughly 72 percent by weight SiO_2, 8 percent CaO, and 20 percent Na_2O (Bates, 1973). Systematic investigations led to the production of an effective pH glass, which is still manufactured and sold under the designation Corning 015. It consisted of 72.2% SiO_2, 6.4% CaO and 21.4% Na_2O (molecular percentages). Modern pH glasses usually contain lithium instead of sodium, providing a much wider measuring range for pH.

Over time the sodium content of a glass electrode will become depleted, causing decreased electrode reponse and E_N potential. Once the electrode potential falls below 95% of the theoretical response (Section 3), the electrode should be regenerated (Section 5.5). If the regeneration is unsuccessful, the probe has been depleted of exchangeable sodium, and should be discarded.

4.3 HYGROSCOPICITY

The degree of sorption of water by the glass membrane of an electrode is termed the hygroscopicity of the glass. Water within the glass lattice structure is essential for the exchange of H^+ and sodium to form the boundary potential. The correlation between the water sorption of a glass and the pH response of electrodes made from the glass is a very direct one (Figure 5).

The application of heat to the glass causes the formation of a non-hygroscopic silica-rich layer. The electrical resistance (E_N, Section 4) of glass electrodes increased 230 percent when the electrodes were dried (Bates, 1973). The resistance returned slowly to its original value when the electrodes were immersed in water. Electrodes made from the lithia-silica glasses are influenced less by drying agents than those of Corning 015 glass. The lithia glasses are known to absorb about one-ninth as much water as do the sodium based glass. Hygroscopicity of a glass membrane can also be destroyed by coating the glass electrode with lacquer or oily substances. The maintenance of the hygroscopicity of the glass electrode is essential for fast and accurate pH measurements.

4.4 GEL LAYER

All glass membranes used in pH electrodes react with water to form a hydrated gel layer (Figure 6). The gel layer is of decisive importance for the performance of a glass electrode as it is the layer that interacts with the hydrogen ions in the sample solution.

Upon hydration of a glass electrode, hydrogen ions in solution exchange with the sodium in the glass to set up a gel layer. As the H^+ ions permeate the gel layer and the lattice structure of the glass electrode, the anionic field strength within the electrode is lowered, allowing sodium ions to diffuse from the glass and the gel layer into the sample solution.

The hydrated glass electrode has two gel layers. The inner gel layer interacts with the internal buffer solution which has a constant hydrogen ion activity and hence potential. The outer gel layer interacts with the hydrogen ions in the sample solution; consequently, the difference between the two potentials (boundary potential) is a function of the pH of the solution.

In solutions containing very low hydrogen ions (pH≧9), the hydrogen ions comprising the gel layer can be exchanged with alkali metals from the solution. Some glass membranes respond to charged alkali metals (e.g. Na^+) under high pH conditions. The exchange of alkali metals (alkaline error) with the gel layer under these extreme conditions cause lower pH values (up to 0.3 pH).

The thickness of the gel layer increases with decreasing temperature because the hygroscopicity of the glass increases with decreasing temperature. The result is a change in the anion field strength and probe response. Under fluctuating temperatures, the gel layer has to establish a new equilibrium with the glass before an accurate pH measurement can be made. Instability of the gel layer leads to sluggish electrode response. The effect of temperature on the gel layer demonstrates the need to stabilize the glass electrode by keeping the temperature of the buffer solutions, the sample solution(s), and the glass electrode uniform.

5. FIELD METHODOLOGY

5.1 SAMPLE COLLECTION

To minimize the interaction of atmospheric CO_2 with the sample solution, the sample container should be filled to exclude air. Rinsing the sample container prior to collection will also help to avoid contamination. pH measurements must be performed within a few hours of collection or stored in a cool dark environment to minimize the effects of biological activity on the sample. Planktonic respiration produces CO_2 (and concomitantly carbonic acid) which will lower the pH of the sample. Photosynthesis by phytoplankton is not a concern if the samples are stored in the dark prior to analysis. The post-sampling biological effects on pH are more of a concern in eutrophic lakes because of the higher plankton biomass.

5.2 TEMPERATURE EFFECTS

Temperature is a very important consideration in the determination of pH because it affects the hydrogen ion activity in the buffer and sample solutions, the hygroscopicity of the glass electrode, and the thickness of the gel layer.

Lower solution temperatures reduce the activity of the hydrogen ion, causing higher pH readings. The effect of temperature on a typical buffer is summarized in Table 1. It must be emphasized that pH electrodes measure the hydrogen ion activity, not hydrogen ion concentration, consequently, buffer readings must be adjusted for temperature.

Lower temperatures increase the hygroscopicity of the glass electrode, which in turn increases the thickness of the gel layer. The gel layer may take 15-30 minutes to reach equilibrium when the temperature is changed significantly (20 → 5°C). pH measurements should not be taken until the gel layer has reached equilibrium.

The increased thickness of the gel layer raises the electrical resistance of the glass, which reduces the response time of the electrode to the sample solution. If the electrical resistance of the electrode exceeds the electrical output of the meter, no pH reading can be made by the meter. Glass electrodes, developed for use in cold environments, use low electrical resistance glass to compensate for the effect of low temperatures on the electrical resistance of the glass electrode.

Hydrogen ion activity declines by approximately 0.01 unit for each 1°C increase in temperature. Thus a sample measured in the laboratory (25°C) will be approximately 0.2 units lower than measurements of the same sample in the field at 5°C (e.g., during winter or in the hypolimnion of a lake). During the summer, when the ambient air temperatures exceed the water temperatures, the glass electrode should be allowed to equilibrate to the water temperature for at least 15 minutes or until the read out is stable. The probe and solutions must be shaded from the direct sun to prevent temperature changes of the test solution during measurement.

Winter sampling poses more difficult problems. Ambient air and water temperatures may be sufficiently cold to inactivate the glass electrode. Samples must be taken to a field laboratory to warm the electrodes and solutions to operating temperatures. Winter sampling may require specialized electrodes. Most suppliers offer a low-temperature glass electrode which are suitable for use to -30°C. A special reference electrolyte will be required for measurements below -10°C (the freezing point of 3M KCl).

The Equithal combination electrode from Ingold Electrodes utilizes a different internal buffer solution which allows a very short response time even when there is a large temperature difference between the electrode and the sample solution. These electrodes are more expensive, but may be desirable under certain field conditions.

Gel-filled reference electrodes are becoming more common, and dry storage can be harmful since the aperture can dry out completely. If the gel becomes dry it may be rehydrated by immersion in a concentrated KCl solution over night. Otherwise there may be an altered liquid junction potential giving rise to unstable readings.

Most manufactures of gel-filled reference electrodes recommend storage in concentrated KCl.

5.5 ELECTRODE REGENERATION

The slope of a glass electrode is a measure of the actual response to hydrogen ion activity (E) versus the theoretical response (E_N calculated using Nernts's equation (Section 4)). The slope is calculated by $(E/E_N) \times 100$. New electrodes should have a slope greater than 98% while old probes should not be used if the slope is lower than 95%. Contamination of the gel layer on the glass electrode or changes in the liquid junction potential are the principal reasons for the reduced slope. The regeneration of the gel layer and the liquid junction potential varies from probe to probe. Check the manufactures specifications and procedures. Some of the more common procedures are outlined below.

Regeneration of the gel layer usually involves immersion of the glass electrode in dilute strong acid (e.g. HCl) for a several minutes. Exposure of the electrode to the dilute acid dissolves some of the aged gel layer. Remove and rinse the electrode, before storing it for 24 hours in a normal storage electrolyte solution. Recalibrate the electrode before using it again.

The most common problem with reference electrodes is zero-point drift, which is a change in the liquid junction potential. The most common causes of zero-point drift are the reference electrolyte becomes contaminated by an ingress of dirt or sample solution, the liquid junction becomes plugged or

contaminated with KCl, AgCl, or AgS precipitates, or the silver chloride has become stripped from the lead-out wire. Regeneration of the reference electrode consists of renewing the reference electrolyte and cleaning the contaminated liquid junction. Check the owners manual for specific instructions of the cleaning procedures for the reference electrode. The stripping of silver chloride from the lead-out resulting in unstable readings, is caused by the use of an incorrect electrolyte. Replacement of the lead-out is a very expensive and complicated procedure, which makes replacement of the electrode more practical.

Regenerated glass and reference electrodes with a slope of less than 95% are beyond further regeneration and should be discarded.

6. STANDARDIZATION OF PROCEDURES

6.1 LITERATURE

pH is a major determining factor in the yield of a chemical process, the rates of growth of organisms, and the solubility of metals. Measurements to determine the effect of pH on these processes from one sample to another have to follow strict guidelines to be comparable with a high degree of reliability. A study by Davison and Gardner (1985) emphasized the need for standardization of procedures in determining pH. In their study, ten participants gathered at one location to compare field and laboratory measurements of the pH of quiescent solutions in natural waters and dilute acids.

Interlaboratory testing at one site showed that standard deviations of measurements on dilute acids and natural waters were generally less than 0.05 pH, and maximum possible bias errors were not usually larger than 0.1 pH. As 95% of all determinations will be within two standard deviations (s.d.) each side of the mean, the maximum error associated with a single measurement of pH will be ±0.2 pH (bias error + 2 s.d.). These results were obtained by laboratories which had been supplied with recommendations regarding equipment and procedures. Focusing of attention on points of detail, and participation in a programme of testing, is sufficient to bring about improvements in accuracy. Therefore, despite any problems caused by the unfamiliar circumstances of the bias tests, the estimate of a total laboratory error of ±0.2 pH is a reasonable assessment of the accuracy which might be achieved routinely when commercial equipment is used.

For field measurements, precision and bias errors were much worse (up to 1 pH unit), apparently because of increased operator error and poor equipment performance (Davison and Gardner, 1985). Electrical equipment marketed specifically for field use can be prone to humidity problems in rain, and the electrodes are selected because of their rugged construction rather than their proven performance. Because pH instability due to CO_2

diffusion enroute to the laboratory, is a recognized problem, high quality field measurements are desirable. In principle, the use in the field of laboratory-grade equipment and well defined analytical procedures should provide the necessary accuracy.

Davison and Gardner (1985) made the following conclusions:

"Considerable bias errors may be due to the preparation of standards, as well as inaccuracies associated with the actual measurement. Undoubtedly, care in the selection and initial testing of electrodes will improve the quality of results. Most important, however, is the unambiguous description of preparation and measurement procedures, and the adoption of routine analytical quality control. The quality of pH data, like those from any other analytical determination, will be greatly improved by strict adherence to a rigorously defined proven routine. Although implementing a programme of quality control will decrease errors, it will not ensure the accuracy of the determination."

The recommended procedures for determination of pH using a glass and reference electrode is outlined in Section 7.

6.2 FIELD AND LABORATORY COMPARISONS

Laboratory and field pH measurements cannot be taken under the same conditions, consequently they are not expected to be the same value. Laboratory measurements from the Environmental Laboratory are assumed to be taken at 1 atmosphere, 22°C, and in equilibrium with atmospheric carbon dioxide. Field pH measurements are taken at ambient temperatures and carbon dioxide concentrations. Altitude and primary productivity can depress carbon dioxide concentrations, while ambient temperatures can be as much as 22°C lower. Decreased ambient temperatures and carbon dioxide concentrations encountered in the field will cause higher pH measurements when compared to the laboratory measurement.

Field pH data determined by a combination glass electrode, pH paper, Hach and Taylor colour comparitors, Surveyor 8000 Hydrolab, and a new relatively inexpensive product, the pH pocket pen were compared to the pH values determined by the Environment Laboratory. The differences between field pH values and Environmental Laboratory pH values are listed in Tables 3 and 4.

Results show the pH pen to have the lowest average and maximum difference. These results may be misleading due to the small sample size and the fact that the pH measurements were taken in the laboratory rather than in the field. The pH pen would certainly be adequate for general, less specific pH measurements (e.g. detection of acid mine drainage). Of the methods commonly used in the field the portable Hydrolab (Surveyor 8000) displayed the lowest average and maximum difference. The new Applied Microsystems Aquamate is expected to have a similar error as it uses the same pH electrode system.

Differences for the combination glass electrode were slightly higher than the differences of the portable Hydrolab. The differences for the Hach and Taylor colour comparitors were 0.2 or 0.1 pH units higher than the average difference of the Hydrolab, and between 0.6 and 0.9 pH units higher than the maixmum difference of the Hydrolab, respectively. The largest deviation between field pH data and lab pH data was found in results determined by the pH paper*. The field pH data measured with the paper showed a 1.2 pH unit average difference from the lab data and maximum differences as large as 2.7 pH units.

A correction factor of 0.01 pH unit was added for every 1°C difference between laboratory temperature (22°C) and the recorded field temperature to allow for temperature induced pH change (Table 4). Comparison of the results show that the addition of the temperature correction factor did not affect the differences between the field pH data and the laboratory pH data.

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*Brand name = ColorpHast sticks

The difference between the field and laboratory pH data were plotted as a function of the laboratory pH (Figures 7 through 11). Figure 7 summarizes the field pH data collected with a Hach kit. The majority of the Hach field pH determinations were less than the laboratory pH, and there was no visual pattern in the variation.

The field pH measurements collected with the ColorpHast pH paper were typically less than the laboratory pH, and there was a distinct increasing bias with increasing pH (Figure 8). These results indicate that the pH paper products are not suitable for field pH measurements.

Field pH measurements collected with the Taylor Comparitor (Figure 9) were usually less than the laboratory pH measurements. There was a general trend for the Taylor Comparitor to overestimate the acid pH measurements, and underestimate the neutral to alkaline field pH measurements. The discrepencies with the Taylor Comparitor were not as drastic as the pH paper, but are sufficiently high as to cause concern regarding the technique.

The combination glass electrode produced field pH measurements that were generally less than the laboratory pH measurements (Figure 10), but no distinct pattern was observed. The Hydrolab (which uses a combination glass electrode) had field pH analyses equally on both sides of the laboratory pH (Figure 11). There was no clear trend in the Hydrolab data.

Based on the results presented, the field pH measurements were usually below the laboratory pH results. The field and laboratory measurements should be routinely compared to provide a check for both procedures. Idealy, the field pH measurements should be slightly higher than the laboratory measurement. Field procedures producing measurements less than, or 0.5 units higher than the equivalent laboratory measurement should be documented and investigated.

7. PROCEDURE FOR pH MEASUREMENT

The following procedure is adapted from those suggested by Bates (1973, pp. 422) and the Department of Biology at Simon Fraser University. It is designed to ensure a high degree of accuracy with the unusual conditions in the field. However, the optimum procedure may vary in detail with the application and the required accuracy (see Bates, 1973). For example, locating acid mine drainage at a mine site requires a pH probe capable of differentiating pH 4 from pH 7. Accuracy to 0.1 pH units is not required for this application. In contrast, very accurate field pH measurements are required to calculate calcite saturation indicies in marl lake.

7.1 PREPARATION

Allow the instrument to warm up thoroughly. If the electrodes have been stored dry, soak in 0.1 M HCl for 2 hours, rinse thoroughly and soak in pH 4 buffer, replacing with fresh buffer periodically, until drift stops.

For reference electrodes with liquid electrolyte, check that the reference electrode is filled and the filling hole is uncovered.

Buffers, sample solutions, wash water, and electrodes should be brought to within 2°C of each other. The electrode temperature can be adjusted by immersing for 10 minutes in a large volume of water having the desired temperature.

All the pH measurements should be taken under quiescent conditions to eliminate error caused by residual streaming potential (McQuaker *et al.* 1983).

Standardization

1. Set the temperature compensation dial to temperature of standard and test solutions.

2. Choose 2 standard buffers whose pH's differ by about 2-3 pH units and which bracket the estimated pH of the sample solution. Use the buffer nearest pH 7 for calibration ("calibration buffer") and the other for adjusting slope ("slope buffer").

3. Rinse electrodes and remove adhering drops with adsorbant tissue without touching the glass membrane.

4. Immerse reference and glass electrodes in the calibration buffer. The entire glass membrane of the glass electrode should be immersed. Do not allow it to touch the beaker.

5. Set function switch to "pH". Set mode switch to normal range (not expanded scale). Some meters have only one operating range.

6. Observe the pH. If present, use the mirror behind the indicating needle to prevent parallax error (align the needle and its reflection by moving your head).

7. Allow drift to decrease to less than 0.005 of a pH unit per minute. This may require several minutes if the electrodes have just been soaking in distilled water.

8. Adjust the calibration knob until the meter indicates the correct pH of the buffer solution at the temperature of the solution (usually room temperature).

9. Set function switch to "stand-by", remove electrodes and replace solution with fresh standard buffer. Do not rinse or blot electrodes.

10. Re-insert electrodes, set switch to "operate" and allow drift to stop (about a minute).

11. Repeat steps 9-10 until the reading is within 0.02 pH units of the correct pH for 2 successive portions of buffer. If several portions are needed the electrodes may not have been initially at the same temperature as the standard.

12. Set meter to "stand-by", remove electrodes, rinse briefly, remove adhering drops and place in the second "slope buffer" solution. Note the pH after drift is negligible (<0.005 unit/min). This should take about a minute.

13. Compare this pH with the correct pH at the temperature of the measurement. Normally the difference should be <0.02 unit. If much greater than this the electrode or meter may be malfunctioning. Small errors in slope can be corrected by adjusting (1) the slope control if present, or (2) the temperature compensator control.

14. Repeat steps 12 and 13 with additional portions of the second standard until successive readings agree within 0.02 unit.

For occasional pH measurements the pH assembly should be restandardized each time. If a series of test measurements are to be done, check the standardization between the first several measurements. If agreement is within 0.02 pH unit, then standardization can be checked less frequently. This will depend greatly on the nature of the test solution. Solutions of some biological materials leave a deposit on the electrode which makes it necessary to wipe the electrode frequently (as in step 3) and restandardize.

7.2 DETERMINING pH - NORMAL PROCEDURE

15. If a weakly buffered solution, such as low ionic strength fresh water, is to be tested see special procedure below (Section 7.3).

16. Set function switch to "stand-by", rinse electrodes well but briefly with distilled water, then remove adhering drops with a tissue without touching the glass membrane.

17. Fill a cup with a portion of the test solution and obtain a preliminary reading of the pH. Repeat without rinsing electrodes until pH is reproducible to ±0.02 unit and drifts less than 0.005 unit per minute.

18. If you are planning more measurements, see the discussion after step 15 and restart either at step 3 or step 15.

7.3 DETERMINING pH: LOW IONIC STRENGTH SAMPLES (<200 µS/cm)

i) Glass and reference electrodes should be designed for low ionic strength conditions. Innovative Electrodes of California have developed a gel-filled reference electrode for use on the Hydrolab and Applied Microsystems multiprobe units which are adequate to 50 µS/cm. Special liquid filled reference electrodes are available from Innovative Electrodes for low ionic solutions ≤ 50 µS/cm. Ingold Electrodes Ltd.[1] is one electrode company specializing in low ionic strength combination electrodes for laboratory use.

ii) Low ionic strength buffers should be used, which can be made up using the procedures in Section 2.

Follow procedure of steps 15-16 except:

a) rinse electrodes additionally with a portion of the test solution.

b) repeat until drifts are less than 0.05 unit/min and successive portions agree within 0.1 unit.

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[1] 261 Ballardvale Street, Wilmington, MA 01998, 617-658-7615

8. CONCLUSIONS

A combination pH electrode works by exchanging sodium or lithium ions with hydrogen ions in solution through an intermediate gel layer associated with the glass electrode. A boundary potential is generated in the glass electrode which is proportional to the hydrogen ion concentration of the sample solution. The boundary potential of the glass electrode when compared to the liquid junction potential of the reference electrode will provide an accurate estimate of the hydrogen ion activity in solution.

The care and storage of glass and reference electrodes is critical to maintain the life and accuracy of the electrodes. Typically the glass and reference electrodes should be stored in the reference electrolyte or, in the case of gel-filled reference electrodes, in concentrated KCl. Glass electrodes should be stored dry for long periods, while reference electrodes should always be stored in the reference electrolyte.

Glass and reference electrodes should be reconditioned when the electrode response to 1 pH unit decreases below 95% of the theoretical response. If the reconditioned response is below 95% the probe should be discarded.

Low temperatures increase the thickness of the gel layer which slows the sodium to hydrogen exchange. As a result, the electrical resistance of the glass electrode increases and response of the electrode to the hydrogen ion activity is slowed. Sample solutions in winter should be warmed to the temperature of the buffers and electrode in a field lab to obtain an accurate reading. The pH taken in the field lab can be corrected to ambient temperature by adding 0.01 pH unit per °C increase.

The liquid junction potential of the reference electrode is influenced by low ionic strength solutions. Low ionic strength pH buffer 4 should be used to eliminate potential liquid junction error when the specific conductance of the sample solution in below 200 µS/cm. Special reference electrodes should be used when the specific conductance of the sample solution is below 50 µS/cm.

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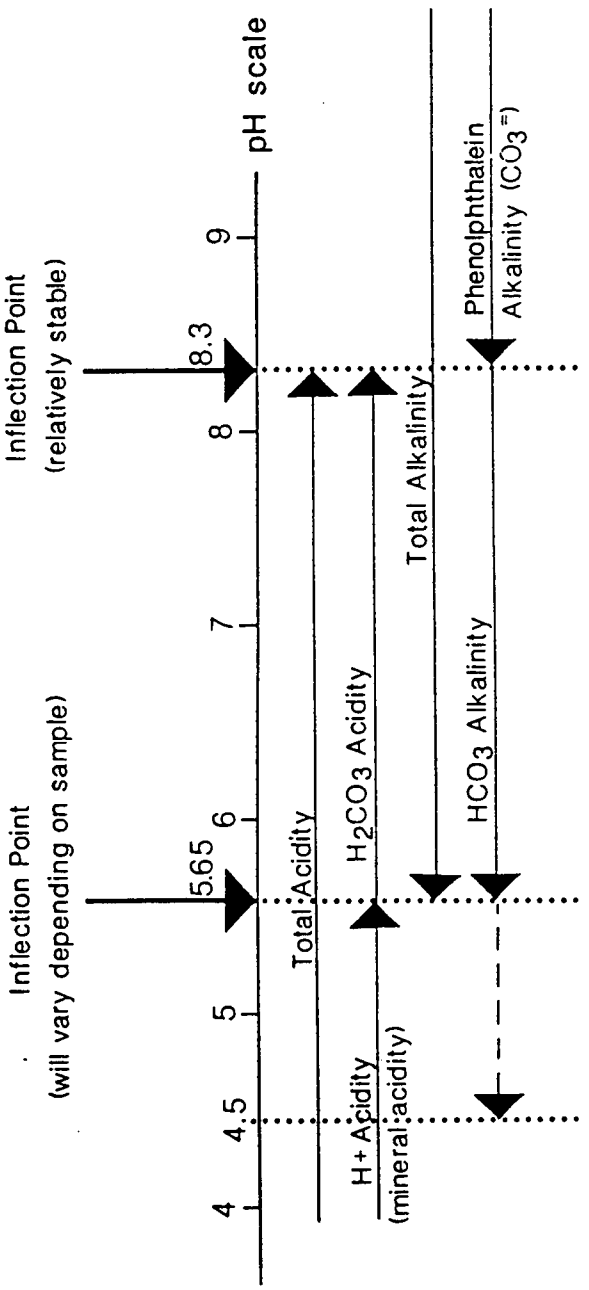


FIGURE 1: pH Scale with Acidity and Alkalinity Terminology

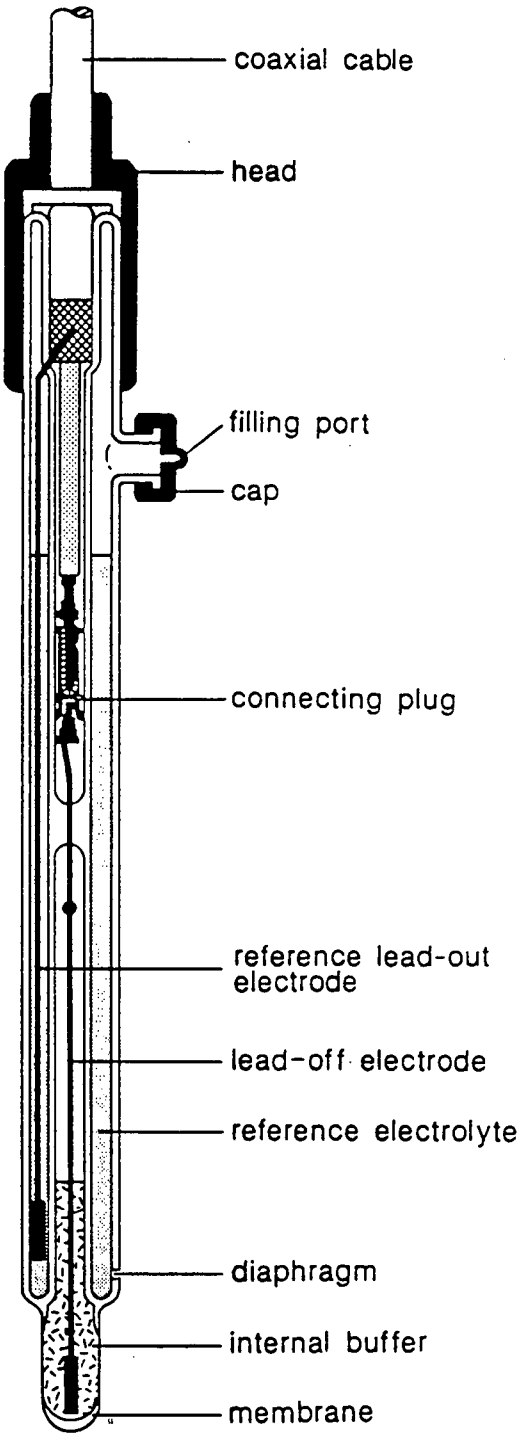
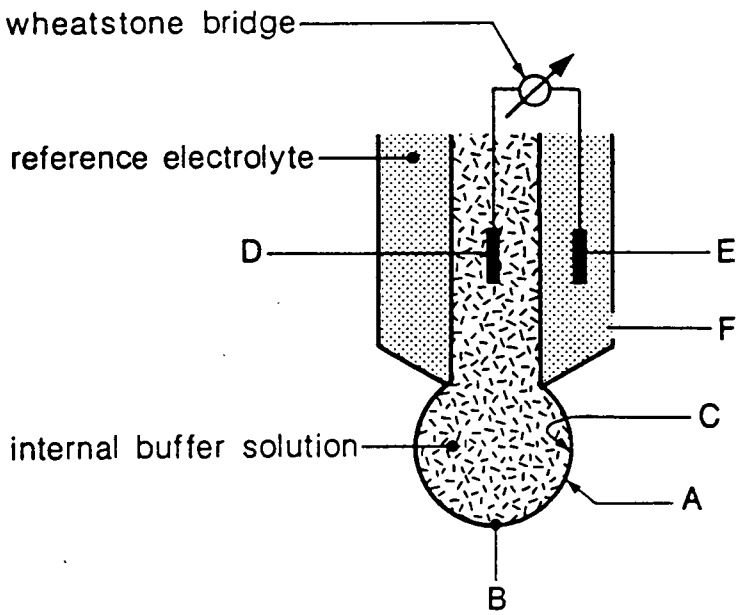


FIGURE 2: Structure of a Typical Combination pH Electrode



A = Potential on outer surface of membrane, dependent on the pH value of the sample solution.

B = Asymmetry (bias) potential, being the potential of the glass membrane with identical solutions and lead-out systems on each side of it. B is determined by the thickness of the glass membrane and by its manufacturing process.

C = Potential on inner surface of glass membrane, depending on the pH value of the internal buffer solution.

D = Potential of the internal Ag/AgCl lead-out electrode, dependent on the a_{Cl^-} value of the internal buffer solution.

E = Reference electrode potential, dependent on the a_{Cl^-} value of the reference electrolyte.

F = Diaphragm or diffusion potential.

FIGURE 3: Electrical Potentials Associated with a pH Combination Electrode

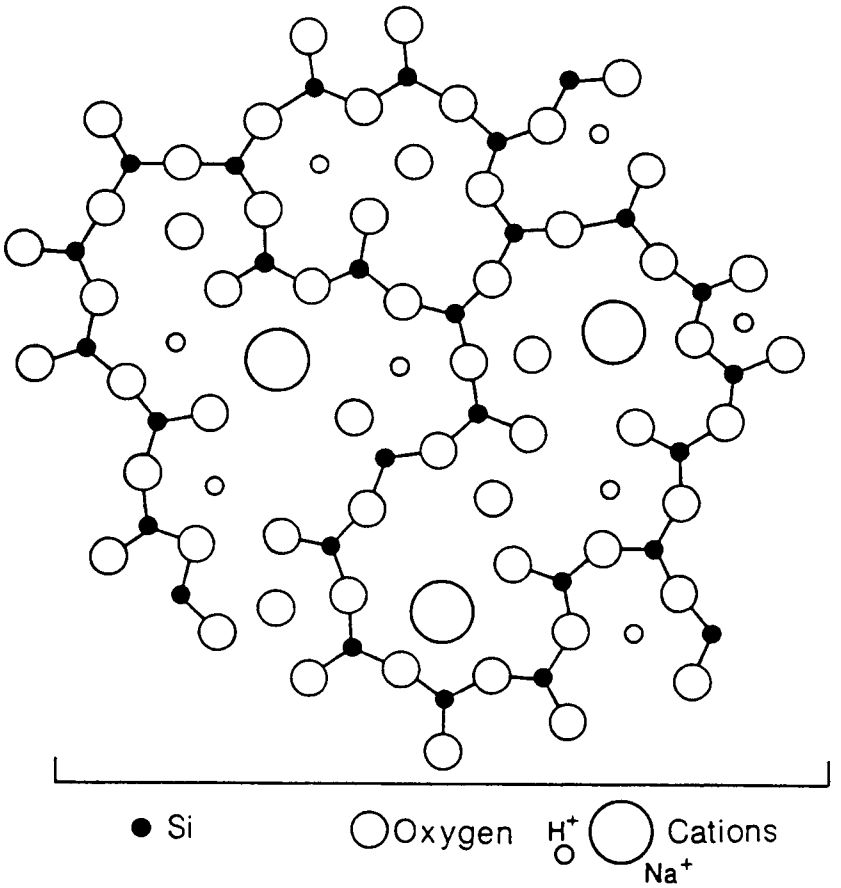


FIGURE 4: Lattice Structure of the Glass Electrode

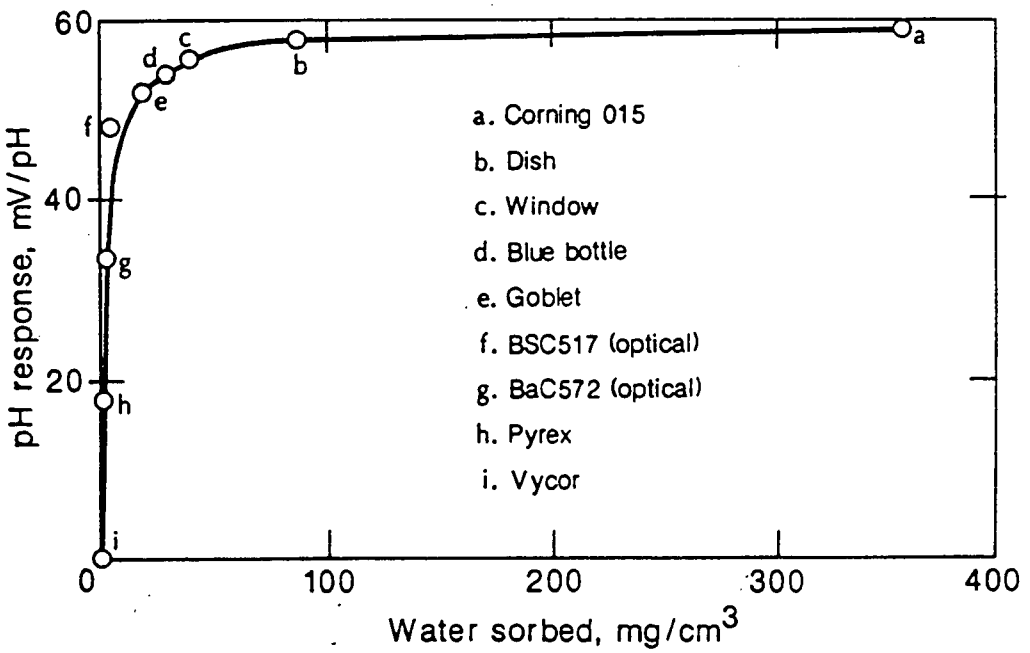


FIGURE 5: Hygroscopicity and pH Response of Nine pH Sensitive Glasses.

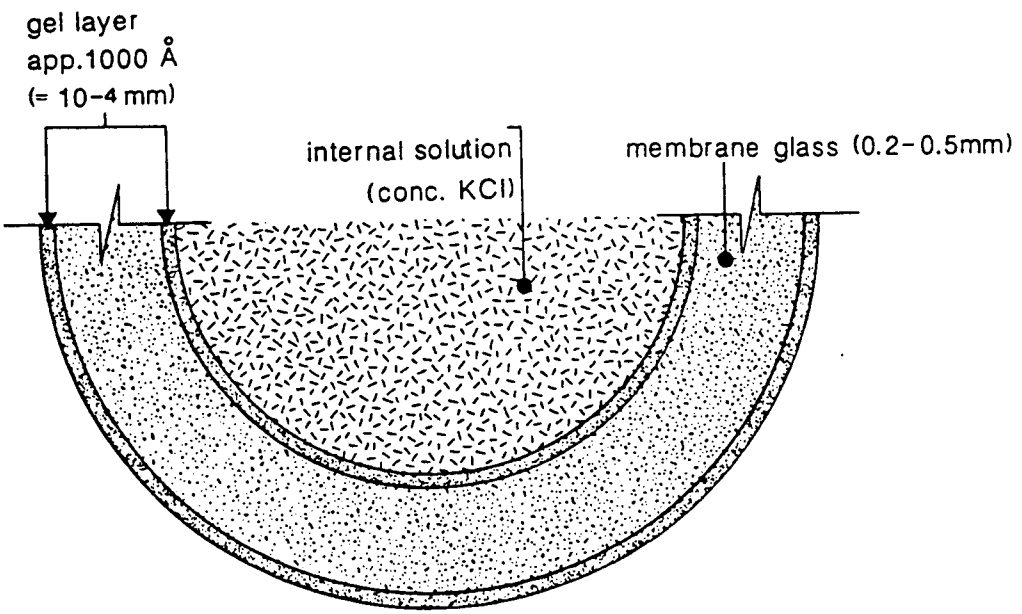


FIGURE 6: Schematic Illustrations of the Structure of a Glass Membrane

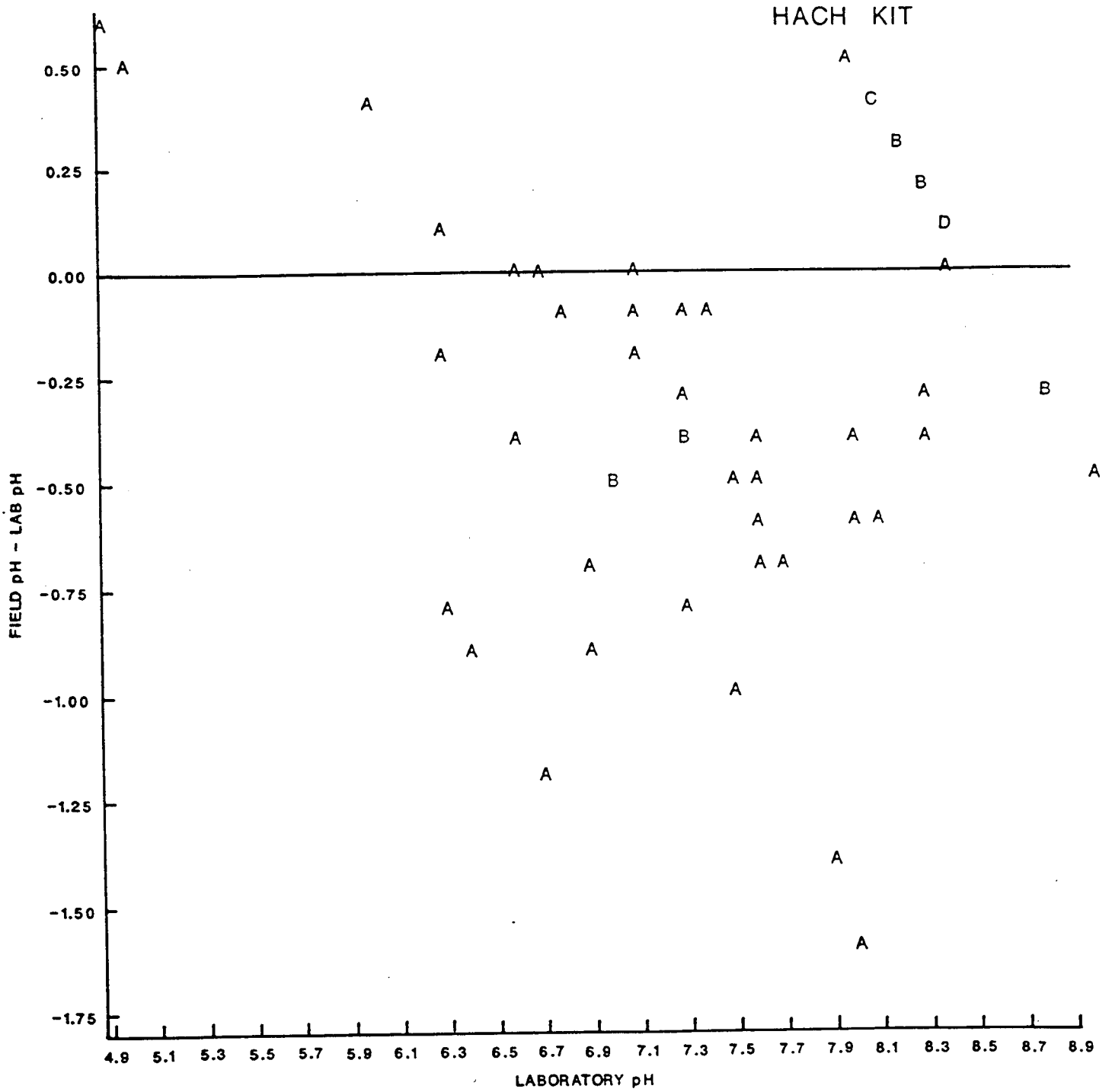


Figure 7: Difference between Hach field pH and laboratory pH as a function of laboratory pH

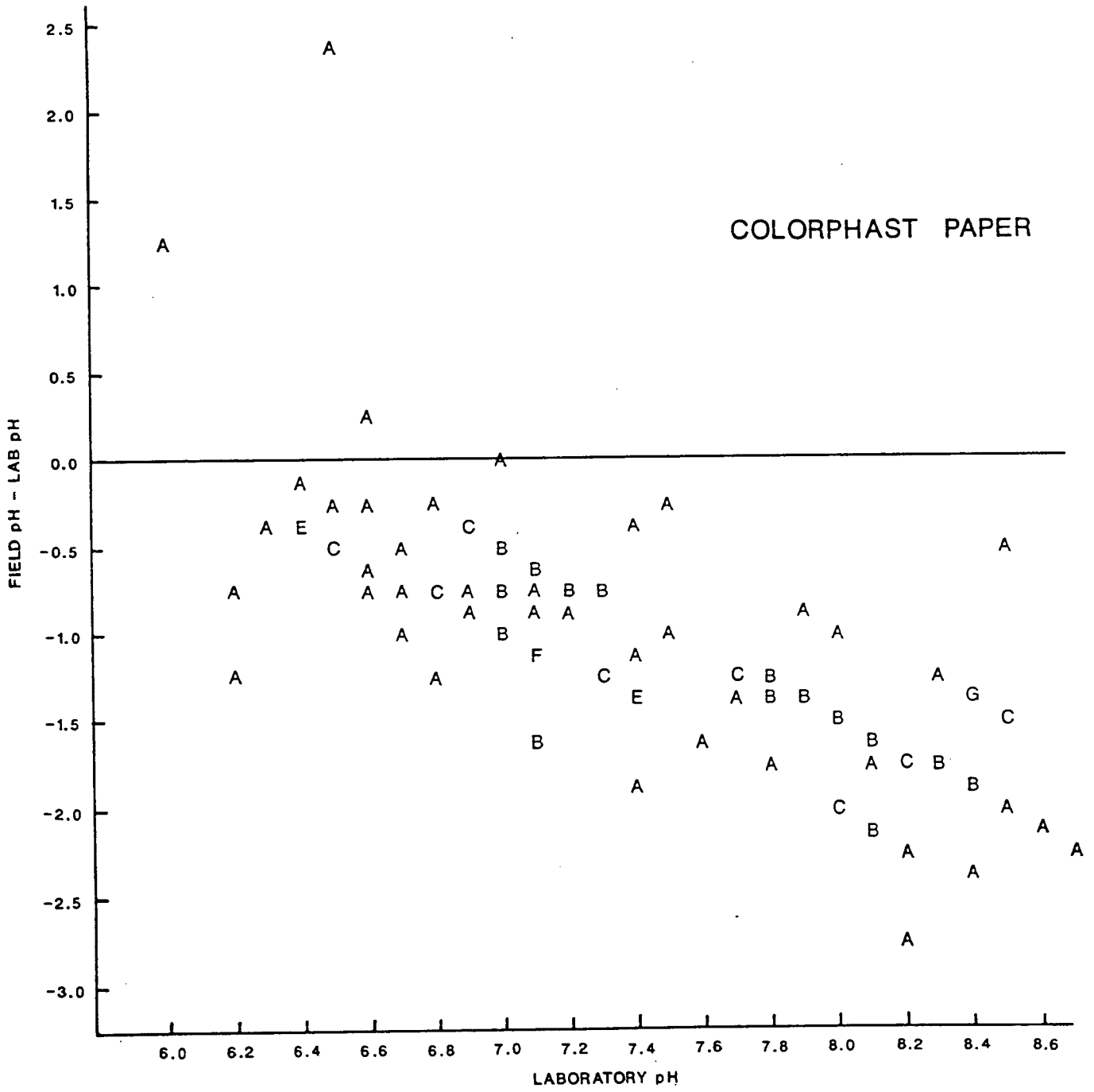


Figure 8: Difference between Colorphast Paper field pH and laboratory pH as a function of laboratory pH

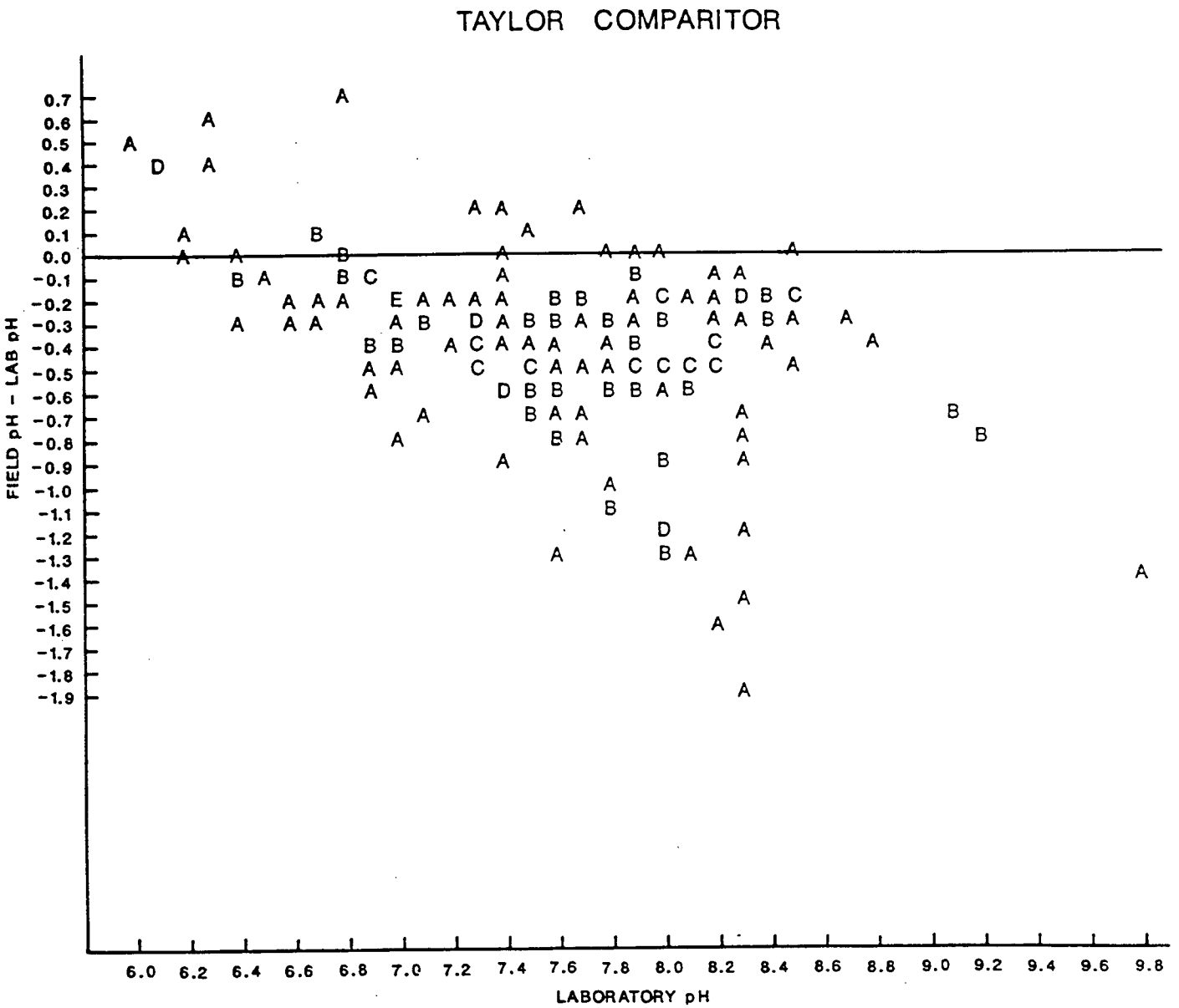


Figure 9: Difference between Taylor Comparitor field pH and laboratory pH as a function of laboratory pH

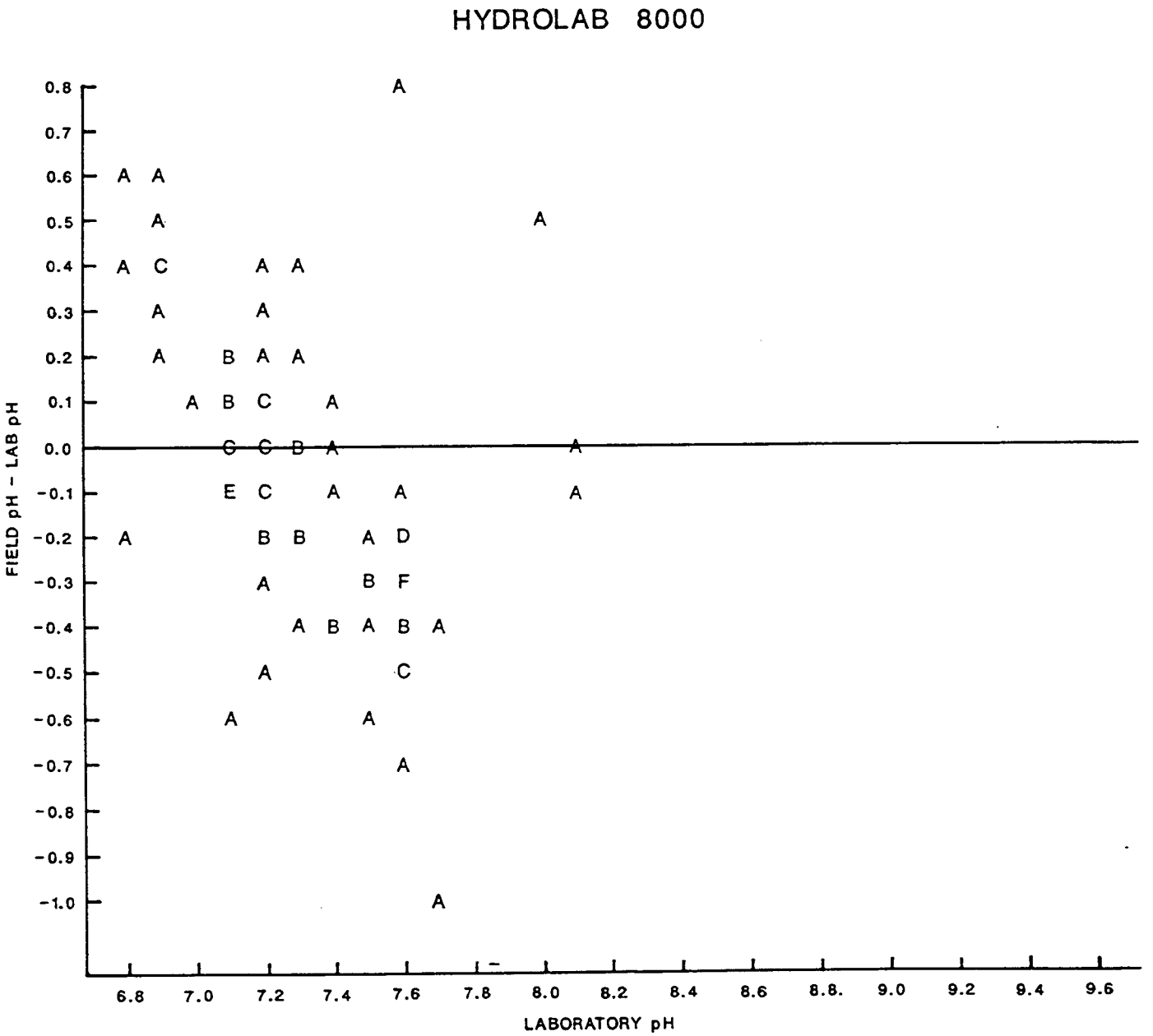


Figure 10: Difference between Hydrolab field pH and laboratory pH as a function of laboratory pH

COMBINATION GLASS ELECTRODE

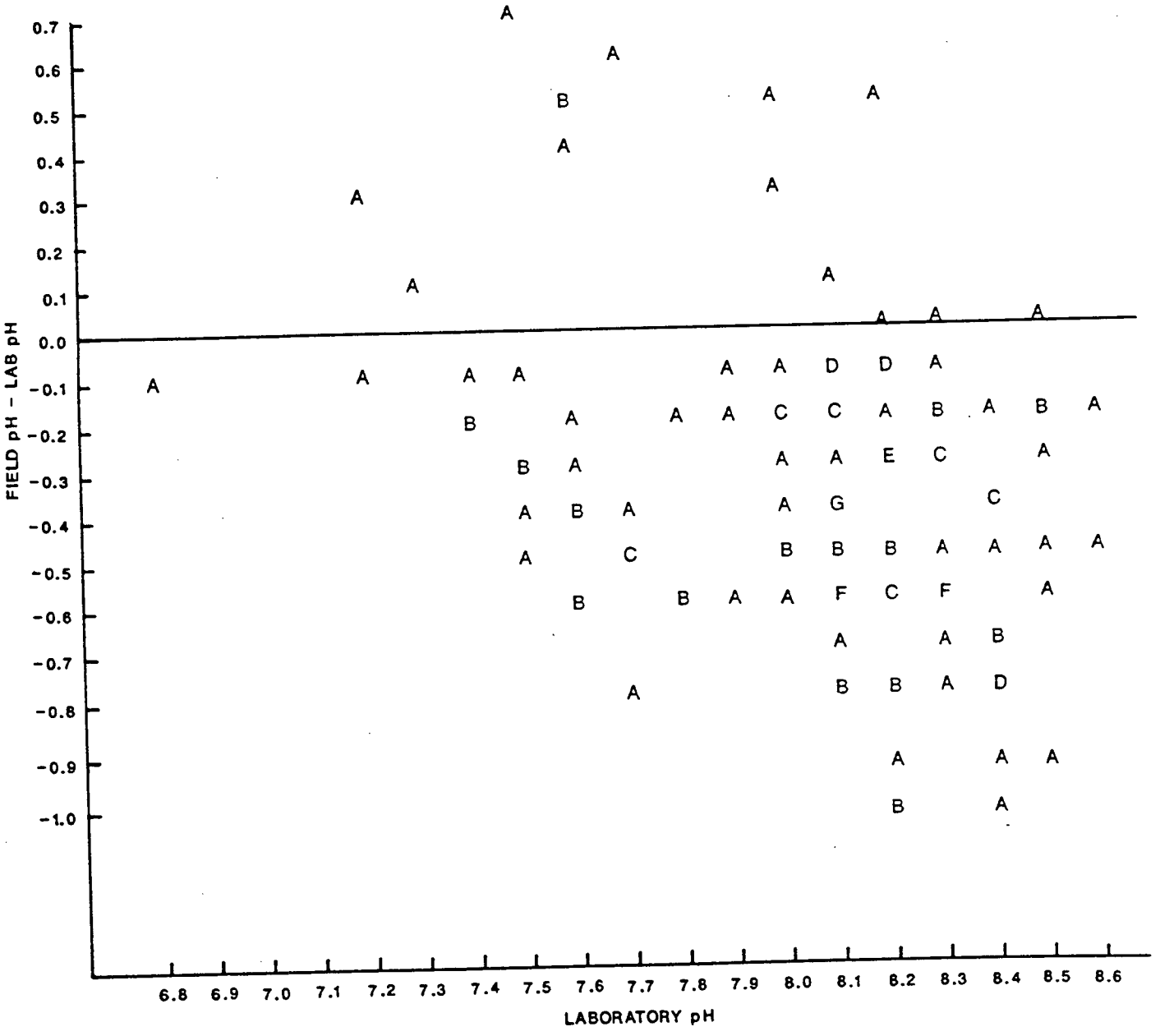


Figure 11: Difference between Combination Glass Electrode field pH and laboratory pH as a function of laboratory pH

TABLE 1

THE pH OF THREE COMMONLY USED BUFFERS AT DIFFERENT TEMPERATURES

Temperature °C	Phthalate	Phosphate	Borate
0	4.01	6.98	9.46
5	4.00	6.95	9.39
10	4.00	6.92	9.33
15	4.00	6.90	9.27
20	4.00	6.88	9.22
25	4.01	6.86	9.18
30	4.01	6.85	9.14

TABLE 2

CHARACTERISTICS OF SOME COMMERCIAL ELECTRODE GLASSES AT 25°C

Designation of Glass or Electrode	Composition of Glass	Glass Resistance (megohms)
Beckman E2	Li_2, 0, BaO, SiO_2	375
Beckman General Purpose	Li_2O, BaO, SiO_2	150
Beckman Amber	Li_2O, BaO, SiO_2	550
Cambridge Standard	Na_2O, CaO, SiO_2	87
Cambridge Alki	Li_2O, BaO, SiO_2	560
Corning 015	Na_2O, CaO, SiO_2	90
Doran Alkacid	Li_2O, BaO, SiO_2	200
Electronic Instruments GHS	Li_2O, Cs_2O, SiO_2	200
Ingold U	--	250
Ingold T	--	140
Ingold UN	Li_2O, SiO_2	30
Jena H	--	105
Jena U	--	30
Jena HT	--	800
Jena HA	--	290
L & N Blue Dot	Na_2O, CaO, SiO_2	50
L & N Black Dot	Li_2O, La_2O_3, SiO_2	70
L & N White Dot	Li_2O, La_2O_3, SiO_2	250
Lengyel 115	Li_2O, BaO, UO_3, SiO_2	15
Metrohm H	Li_2O, BaO, SiO_2	1400
Metrohm X	Li_2O, CaO, SiO_2	100
Metrohm U	Li_2O, BaO, SiO_2	500

TABLE 3

DIRECT COMPARISON OF FIELD AND LABORATORY pH DATA

Method	No. of Records	Average Difference*	Standard Deviation	Median	90th Percentile	Maximum Difference
Combination Glass Electrode	415	0.4	0.24	0.4	0.8	1.0
HACH Comparitor	55	0.4	0.34	0.4	0.8	1.6
ColorpHast Sticks	118	1.2	0.58	1.2	1.9	2.7
Taylor Comparitor	189	0.5	0.34	0.4	0.9	1.9
Hydrolab	83	0.3	0.20	0.2	0.5	1.0
Hach Pocket Pen	40	0.135	0.14	0.1	0.3	0.5

*absolute difference between laboratory pH and field pH.

TABLE 4

COMPARISON OF FIELD AND LABORATORY pH DATA AFTER CORRECTING FOR TEMPERATURE DIFFERENCES

Method	No. of Records	Average Difference*	Standard Deviation	Median	90th Percentile	Maximum Difference*
Hach Comparitor	52	0.4	0.34	0.4	0.8	1.7
ColorpHast Sticks	116	1.1	0.59	1.1	1.9	2.8
Taylor Comparitor	179	0.5	0.33	0.4	0.9	2.0

*absolute difference between laboratory pH and temperature corrected field pH.

APPENDIX 1

Anion/Cation Balance in Fresh Water
(from Riehl, 1971)

The accuracy of an analysis may be estimated by comparing the sum of the milliequivalents per litre (me/L) of the positive radicals (cations) with the sum of the milliequivalents per litre of the negative radicals (anions). In a perfect analysis they would be exactly the same. The percentage of error may be figured readily by the Stabler formula:

$$e = \frac{rp-rn}{rp+rn} \times 100$$

e = percentage of error
rp = sum of me/L of positive radicals
rn = sum of me/L of negataive radicals

The milliequivalts per litre are determined as follows:

$$\text{me/L} = \text{mg/L of element or compound (found by analysis)} \times \frac{\text{Valence}}{\text{Atomic Weight}}$$

Conversely, if results are expressed as milliequivalents per litre, milligrams per litre are determined as follows:

$$\text{mg/L} = \text{me/L} \times \frac{\text{Atomic Weight}}{\text{Valence}}$$

The following table shows the coefficients for converting milligrams per litre (mg/L) into milliequivalents per litre (me/L):

Positive Radicals		
mg/L Calcium	(Ca)	x 0.0499 = me/L
mg/L Magnesium	(Mg)	x 0.0823 = me/L
mg/L Sodium	(Na)	x 0.0435 = me/L
mg/L Potassium	(K)	x 0.0256 = me/L
mg/L Manganese	(Mn)	x 0.0364 = me/L
mg/L Hydrogen	(H)	x 0.9921 = me/L

Negative Radicals

mg/L Carbonate	(CO_3)	x 0.0333 = me/L
mg/L Bicarbonate	(HCO_3)+	x 0.0164 = me/L
mg/L Sulphate	(SO_4)	x 0.0208 = me/L
mg/L Chloride	(Cl)	x 0.0282 = me/L
mg/L Fluoride	(F)	x 0.0526 = me/L
mg/L Nitrate	(NO_3)	x 0.0161 = me/L

The following table shows the coefficients for converting me/L into mg/L.

Positive Radicals

me/L Calcium	(Ca)	x 20.04 = mg/L
me/L Magnesium	(Mg)	x 12.16 = mg/L
me/L Sodium	(Na)	x 23.00 = mg/L
me/L Potassium	(K)	x 39.10 = mg/L
me/L Manganese	(Mn)	x 27.46 = mg/L
me/L Hydrogen	(H)	x 1.01 = mg/L

Negative Radicals

me/L Carbonate	(CO_3)	x 30.00 = mg/L
me/L Bicarbonate	(HCO_3)	x 61.01 = mg/L
me/L Sulphate	(SO_4)	x 48.03 = mg/L
me/L Chloride	(Cl)	x 35.46 = mg/L
me/L Fluoride	(F)	x 19.00 = mg/L
me/L Nitrate	(NO_3)	x 62.01 = mg/L

Reporting results in terms of positive and negative radicals does not always satisfy the layman for it gives him a hazy impression of the composition of the water; therefore the results may be reported according to a graphic scheme or a possible hypothetical combination.

+Bicarbonate alkalinity expressed as 1.22 X (T-2 Phenothaline Alkalinity)

Graphic Scheme

Graph the milliequivalents/L using the following conventions. The length corresponding to the calculated milliequivalent is graphed in two columns, the cations in the first column and the anions in the second. The anions and cations should be arranged according to a recognized system of pairing. Use the order of positive and negative radicals outlined previously.

The graph provides a visual assessment of the ionic pairs, and anion/-cation balance which is a fundamental requirement in any freshwater study.

pH MEASUREMENTS

G. Bruce Holms

British Columbia

Ministry of Environment, Lands, and Parks

MINISTRY OF ENVIRONMENT, LANDS and PARKS
PROVINCE OF BRITISH COLUMBIA

COMPARISON OF ANALYTICAL METHODS FOR pH USED IN THE LAKE TREND MONITORING PROGRAM

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OCTOBER, 1993

Executive Summary

This report describes the analytical precision of two methods of measuring pH—the Orion Ross combination pH electrode method and the Metrohm automated electrode method—in ambient water samples. The study involved:

- a comparison of precision measurements for each method to the Long Range Transport of Air Pollutants (LRTAP) interlaboratory acceptable error values, and to the U. S. Environmental Protection Agency intralaboratory precision objective;
- an evaluation of the effect of calibration methods on analytical variability;
- an evaluation of the change in reported pH values over time;
- an evaluation of the interaction between the sample and the atmosphere and it's effect on pH variability; and
- an evaluation of the data management methods for reported pH values.

Ionic strength of ambient water quality samples determines the analytical procedure used to measure pH. We recommend that:

- the Orion Ross combination pH electrode method be used with the 60-mL syringe sampling method for data required to meet the LRTAP criterion for interlaboratory acceptable error values or the EPA intralaboratory precision objectives.

- the conductivity of ambient water quality samples should be used to indicate ionic strength. If the conductivity of ambient water quality samples is less than 1000 uS/cm, then the Orion Ross combination pH electrode method should be used. The Metrohm automated electrode should only be used for high ionic strength samples or when low ionic strength solutions have been used in the calibration procedure.

- water samples be analyzed for pH as soon as possible to minimize changes in pH values caused by gas exchange.

- reported values for pH using the two analytical methods be stored separately and evaluated separately.

- a data quality flag be associated with all values that were analyzed immediately after the Metrohm automated electrode was calibrated.

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1 INTRODUCTION

The Lake Trend Monitoring Program has used two analytical methods for measuring pH in ambient water samples and used two methods for collecting these samples. This report assesses the analytical methods and sampling methods, and recommends how future measurements of pH in ambient water samples should be sampled, analyzed, and stored in a database.

The purpose of the Lake Trend Monitoring Program is to assess the long-term effects of acid deposition on water quality and aquatic life (Swain 1991). Ambient water samples are collected monthly from four lakes located on Vancouver Island, one lake located on Saltspring Island, and one lake located on the lower mainland of B.C. The Quality Assurance and Quality Control (QA\QC) sampling portion of this program includes samples containing de-ionized water and ambient water. The de-ionized water is added to the 1-L sample bottle and sent to the laboratory for analysis. Ambient lake samples are collected from the six lakes, with the use of a 1-L sample bottle and a 60-mL syringe, and sent to the laboratory.

The monitoring program uses two analytical methods to measure pH (Dr. D. Jeffery, pers. comm.).[1] The Metrohm automated electrode consists of a glass indicating electrode and a platinum reference electrode. The electrodes are placed into the water sample and allowed to stabilize (i.e., allows the sample to interact with the indicating electrode and allows the electrode to compensate for the temperature of the sample) for a fixed period of time. The pH value is reported two minutes later. The electrodes are removed from the sample, rinsed in de-ionized water, and placed in the next water sample for analysis. Calibration of the reference electrode is done at the beginning of the day with solutions of pH 4 and 7. Samples with known pH values of 4, 7, and 10 are used to verify the accuracy of the readings from the electrode. Analyses of these samples are performed as required.

The Orion Ross combination pH electrode method is a manual method used to measure pH in water samples. Two aspects of this method differ from the Metrohm automated electrode method. First, the Orion Ross combination pH electrode method uses a stabilization period which varies with each sample. Second, the calibration method for the Orion Ross combination pH electrode is expanded to include pH 10.

Two methods of sample collection are used in this program. Water quality samples were collected with a 1-L sample bottle and with a 60-mL syringe. The syringe was used to minimize the amount of interaction between the sample and the atmosphere. These interactions may contribute to the variability in reported pH values.

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[1] Details of the two analytical methods and calibration method were provided by Dr. D. Jeffery (Zenon Enviromental Laboratories) to Mr. G. B. Holms (Water Quality Branch) on September 17, 1991 and May 20, 1992.

2 EXPERIMENTAL DESIGN

A "repeated measures" design was adopted to compare the two analytical methods and two sampling methods used for pH. This type of experimental design compares the difference between values that are collected sequentially. The difference may be measured within a series of values (e.g., the difference in pH values between sequential samples from a lake) or between a series of values (e.g., the difference in pH values reported over time). This assessment compared:

- the difference between reported values of pH from the two analytical methods,
- the variability in reported values of pH for each analytical method (i.e., standard deviation was used to expressed variability),
- the difference in reported values of pH over time for each analytical method, and
- the difference between reported values of pH from the two sampling methods.

The difference between reported values of pH from the two analytical methods was evaluated using a Student's paired *t-test* and the Long Range Transportation of Air Pollutants acid rain QC interlaboratory criterion for acceptable error between reported values (0.25) (Arafat and Aspila 1990). The pH values reported by the two analytical methods are considered *unique* when the *t-test* indicates that the differences are significant or when the difference exceeds the criterion.

The purpose of examining the variability within each analytical method was to determine the randomness of the error measurement. The distribution characteristics (i.e., normality, kurtosis, skewness) of repeated pH measurements were used to describe the variability in reported values of pH for each analytical method. A normal distribution is characterized by a constant mean value with no variability. If this is not the case, skewness and kurtosis are used to describe the shape of the distribution of values. This type of variability was also examined in this report using the U. S. Environmental Protection Agency intralaboratory precision objective (standard deviation for replicate samples in a laboratory should be $\leq$ 0.05 pH units) (Silverstein et al 1987) and Grubb's test for outliers (Taylor 1987). Values for pH reported by an analytical method are considered *unreliable* when the standard deviation is not normally distributed, contains outliers, or exceeds the objective.

A Student's paired *t-test* was used to evaluate the differences in pH values over time for ambient water analyzed by the two analytical methods. Values for pH reported by an analytical method are considered *unreliable* when the *t-test* indicates that the differences over time are significant.

The difference in reported pH values between the two sampling methods, for ambient water, was evaluated using a Student's paired *t-test.* Values for pH reported by a sampling method are considered *unique* when the *t-test* indicates that the differences are significant.

The purpose of using de-ionized water was to reduce the sources of variability in samples by minimizing the interactions between ions within the sample and their effect on the reported pH value. Buffering capacity of de-ionized water was not considered in the selection of this sample medium. Ten de-ionized samples (collected on September 21, 1990, and reported in Table 1 and

Figures 1 and 2) were used in these comparisons. The ionic strength of these samples and their reported pH values were lower than for the samples from ambient lakes. Therefore, additional ambient water samples were collected on four occasions to verify the results of the comparisons made using de-ionized water: September 21, 1990 (Table 1, Figures 1 and 2), November 8, 1990 (Table 2, Figures 3 to 6), and February 14 and August 2, 1990 (Table 4, Figures 7 and 8).

Samples collected from Maxwell Lake on February 14 and August 2, 1990, were used to compare the difference between sampling methods. These data are presented in Table 4 and Figures 7 and 8.

A comparison between evaluations using the reported pH values and those using an antilog transformation of the pH values indicated that the evaluations were similar. For clarity, the presentation of the comparisons uses the reported pH values.

3 VARIABILITY IN REPORTED pH VALUES FOR DE-IONIZED WATER

In September 1990, ten 1-L samples of de-ionized water were opened, sealed, and labelled over the course of the sampling trip: three samples at the start of the trip (labelled as "Sample 1 Day 1 Pre-Maxwell Lake"), four over the course of the sample trip (three samples were labelled as "Sample 1 Day 2 Pre-Maxwell Lake" and one sample was labelled as "Pre-Maxwell"), and three samples at the end of the sampling trip (labelled as "Sample 1 Day 1 Post Old Wolf Lake"). All the samples were analyzed for pH using the Orion Ross combination pH electrode method and the Metrohm automated electrode method. These samples were then re-analyzed three days later using the Orion Ross combination pH electrode method. The pH values reported from these samples were tabulated in Tables 1 and 3 and presented in Figures 1 and 2.

3.1 Comparison of Analytical Methods

The differences in pH values between the two analytical methods are shown in Table 1 and Figure 1. Seven of the 10 samples reported higher values for pH when analyzed by the Orion Ross combination pH electrode method than when analyzed by the Metrohm automated electrode method.

The difference in pH values between the two analytical methods ranged from 0.055 to 0.623, with a mean difference of 0.147 and a standard deviation of the differences of 0.17. A paired Student's *t-test* ($p = 0.023$) confirmed that the two analytical methods produced different results.

The LRTAP acid rain QC interlaboratory study lists an acceptable error of 0.25 between reported values (Arafat and Aspila 1990). This value was applied to the difference between pH values reported by the two analytical methods. In one sample, Sample 1 Day 2 Pre-Maxwell Lake, the difference (0.623) between pH values reported by the two analytical methods exceeded the acceptable error value. The influence of the difference between this one pair of pH values (6.268 measured by the Metrohm automated electrode and 5.645 measured by the Orion Ross electrode)

was sufficient for the *t-test* to conclude that the results from these analytical methods were different.

3.2 Variability within Analytical Methods

The variability of pH values analyzed using the Metrohm automated electrode method (standard deviation, 0.239) was greater than the variability in values analyzed using the Orion Ross combination pH electrode method (Table 1). The latter showed very little variability (standard deviation, 0.021).

A Grubb's test for outliers (Taylor 1987) identified the first value reported for the Metrohm automated electrode method as an outlier ($T_{(10)}$ =2.665, probability of the value not being an outlier : $p < 0.1\%$).

The U.S. EPA intralaboratory precision objective (the standard deviation $\leq$ 0.05 pH units)(Silverstein et al 1987) was exceeded by values analyzed by the Metrohm automated electrode method. Even after the outlier identified by the Grubb's test was removed from the data series, the variability (0.089) remained four times greater than that found using the Orion Ross combination electrode method (0.021) and exceeded the U.S. EPA intralaboratory precision objective (the standard deviation $\leq$ 0.05 pH units). These facts suggest that the difference between pH values reported by the two analytical methods is primarily a function of the variability in values reported by the Metrohm automated electrode method.

The randomness of variability in pH values reported by each method was evaluated and presented (Table 3, Figures 1 and 2). The pH values for de-ionized water analyzed using the Orion Ross combination pH electrode method were normally distributed about the sample mean (p=0.44). However, the shape of the distribution differed from that of a normal distribution (e.g., Bell curve) by having more values occurring in the intermediate region of the distribution than near the mean or tails ("platykurtic distribution"), and that the pH values for the intermediate region were less than the mean of the distribution ("positively skewed"). Reported values for pH using the Metrohm automated electrode method were not normally distributed about the sample mean ($p < 0.01$). This reflects the influence of the first sample analyzed. This distribution differed from a normal distribution by having more reported values occurring near the mean and tails than in the intermediate regions ("leptokurtic distribution"), and were positively skewed.

3.3 Variability over Time

The water samples were analyzed for pH using the Orion Ross combination pH electrode method and then re-analyzed three days later (Table 1 and Figure 2). Reported pH values increased over time (mean value Day 0, 5.62; mean value Day 3, 5.64) with a mean difference of 0.021 and standard deviation of 0.017. The results of the *t-test* indicated that pH values reported on Day 0 differed from those reported on Day 3 (p= 0.041).

4 VARIABILITY IN REPORTED VALUES OF pH FOR AMBIENT LAKE WATER

Ambient water samples were analyzed for pH using the two analytical methods in 1990. A sample was collected from each of the three lakes (Maxwell Lake, Stocking Lake, and Spectacle Lake) in September, and 32 samples were collected from four lakes (Maxwell Lake, Stocking Lake, Old Wolf Lake, Spectacle Lake) in November. The pH values reported from these samples were tabulated in Tables 1 and 2 and are presented in Figures 3 to 6. The November series of samples were re-analyzed by the Metrohm automated electrode to compare changes in pH values over time. Six samples collected from one lake (Maxwell Lake) in February and in August were used to evaluate the difference between the sampling methods. The pH values reported from these samples are presented in Figures 7 and 8 and Table 4.

4.1 Comparison of Analytical Methods

A comparison of analytical methods was made using pH values from 1-L bottle samples. Values for pH analyzed using the Orion Ross combination pH electrode method were consistently higher than those analyzed using the Metrohm automated electrode method for samples collected in September, November, and February. In August, values for pH using the Metrohm automated electrode method were higher than those reported using the Orion Ross combination pH electrode method. The difference in pH values between analytical methods for ambient lake samples ranged from 0.215 to 0.528 in September, from 0.027 to 0.27 in November, from 0.08 to 0.21 in August, and from 0.011 to 0.147 in February.

The results of the *t-test* indicated that the pH values reported by the two analytical methods were significantly different (November: p=0.0001, p=0.007; August: p=0.0012, February: p=0.0042).

The acceptable error of 0.25 between reported values, set by the LRTAP acid rain QC interlaboratory study (Arafat and Aspila 1990), was approximated on one occasion in November and exceeded on three occasions, twice in September and once in November.

4.2 Comparison of Sampling Methods

A preliminary comparison between pH values reported for the 60-mL syringe sample method and those of the 1-L bottle sample method was done at each lake in November 8, 1990 (Table 2 Figures 3 to 6). In this comparison, pH values from eight 1-L samples were compared to one value from a 60-mL syringe sample. The comparison showed that the pH from the 60-mL syringe sample:

- was approximated by the mean pH value reported using the Orion Ross combination pH electrode method for 1-L samples collected in Maxwell Lake;
- was greater than those reported using either the Orion Ross combination pH electrode method or the Metrohm automated electrode method for 1-L samples collected in Stocking Lake and in Old Wolf Lake; and
- was greater than those reported using the Metrohm automated electrode method and less than those reported using the Orion Ross combination pH electrode

method in 1-L samples collected in Spectacle Lake.

The differences between pH values reported by the two sampling methods were greatest when the samples were analyzed by both analytical methods (i.e., 1-L samples analyzed with the Metrohm automated electrode method and 60-mL syringe samples analyzed with the Orion Ross combination pH electrode method). The differences in pH values reported for 1-L bottle samples analyzed by the Metrohm automated electrode method and 60-mL syringe samples analyzed by the Orion Ross combination pH electrode method were similar to the differences reported between analytical methods for samples collected in November and for de-ionized water samples in September. These results indicate that sample method and analyzing method have a compounding effect on the reported pH values.

The pH values reported for samples analyzed using the Orion Ross combination pH electrode method were combined (eight values reported using 1-L sample method and one reported value using the 60-mL syringe sample method) and presented in Figures 3 to 6. A Grubb's test for outliers (Taylor 1987) identified the value reported using the syringe sample method from Spectacle Lake was an outlier ($T_{(8)}$=2.31, risk of false rejection 5%). This preliminary comparison indicates that the sampling method has an effect on pH values.

A second comparison of the pH values reported by the two sample methods is presented in Table 4, and Figures 7 and 8. This comparison evaluates pH values reported from replicate samples using the two sample methods (1-L bottle samples and the 60-mL syringe samples). The acceptable error of 0.25 between reported values, set by the LRTAP acid rain QC interlaboratory study was exceeded by one value in August (0.27). This difference was between the value reported for a 1-L bottle sample analyzed using the Metrohm automated electrode method and the value reported for a 60-mL syringe sample analyzed using the Orion Ross combination pH electrode method. The U.S. EPA intralaboratory precision objective (the standard deviation ≤ 0.05 pH units) (Silverstein et al 1987) was exceeded by 1-L bottle samples analyzed using the Metrohm automated electrode method (standard deviation, 0.055) and by 60-mL syringe samples analyzed with the Orion Ross combination pH electrode method (standard deviation, 0.063) collected from Maxwell Lake in August.

The results of the paired Student's *t-test* concluded that:

- The pH values reported for 1-L bottle samples analyzed using the Metrohm automated electrode method were different than those values reported for 60-mL syringe samples analyzed by the Orion Ross combination pH electrode method (August samples, p=0.0001; February samples, p=0.002).
- The pH values reported for the 1-L bottle samples and the two analyzing methods were different (February samples, p=0.004; August samples p=0.001).
- The pH values reported for 1-L bottle samples analyzed using the Orion Ross combination pH electrode method were similar to values reported for 60-mL syringe samples analyzed using the Orion Ross combination pH electrode method in February (p=0.11). The values reported by these sampling procedures were different in August (p=0.023).

In the two comparisons, a larger difference between pairs of pH values was observed when both the sampling methods and the analytical methods were different. This difference is reduced when the two sampling methods are analyzed using the Orion Ross combination pH electrode method. The replicate sampling comparison indicated that the sampling method had a minor effect on reported pH values compared to the analytical method.

4.3 Variability within Analytical Methods

A comparison of variability within analytical methods was made using pH values from 1-L bottle samples. The variability within analytical methods was lower in samples analyzed by the Orion Ross combination pH electrode method than in samples analyzed by the Metrohm automated electrode method (Tables 2 and 4). Variability, expressed in terms of standard deviations, ranged from 0.015 to 0.027 using the Orion Ross combination pH electrode method, and from 0.03 to 0.055 using the Metrohm automated electrode method.

The U.S. EPA intralaboratory precision objective for replicate samples analyzed in a laboratory (standard deviation of 0.05 pH units) was exceeded by values from the 60-mL syringe samples collected from Maxwell Lake in August 1990 and analyzed using the Orion Ross combination pH electrode method. The objective was also exceeded by values from replicate 1-L bottle samples collected from Maxwell Lake in August 1990 and analyzed using the Metrohm automated electrode method. However, these results were reported to one significant figure rather than two or three significant figures used for all the other analyses. For this reason the results reported for replicate 1-L bottle samples collected from Maxwell Lake in August 1990 and analyzed using the Metrohm automated electrode method have been excluded from this comparison. Factors which could cause variability to exceed this objective are:

- the low ionic strength of the lake samples,
- the calibration methods of the electrodes, and
- the period of time the indicating electrode is exposed to the sample before a reading is made (i.e., the time period is predetermined for all samples analyzed by Metrohm automated electrode method, whereas this time period varies for samples analyzed by the Orion Ross combination pH electrode method).

Ionic strength of a lake sample can be determined by the formula:

$$I = 1/2 \sum_i Z_i^2 \, (S_i)$$ where (S_i) is the molar concentration of S_i and Z_i is the charge number of the ion.

or by measuring the conductivity of the sample.

The ionic strength of the lake samples (Old Wolf Lake, 2.54×10^{-4} moles/L or 36 uS/cm; Stocking Lake, 3.55×10^{-4} moles/L or 38 uS/cm; Spectacle Lake, 5.45×10^{-4} moles/L or 58 uS/cm; Maxwell Lake, 6.18×10^{-4} moles/L or 60 uS/cm) were three orders of magnitude lower than the ionic strength of the buffer solutions (pH 4, 0.5 moles/L or 4740 uS/cm; pH 7, 0.14 moles/L or 8290 uS/cm; pH 10, 0.116 moles/L or 6190 uS/cm) used to calibrate the electrode. This difference may contribute to a lower pH value being reported by the electrodes in two ways.

First, the hydrogen ions will not dissociate as freely when in a high ionic strength solution to a weaker ionic strength solution. Second, time required for the sample to equilibrate may be greater than the predetermined time that the sample is exposed to the indicating electrode when using the Metrohm automated electrode method.

The method for analyzing pH in ambient water lake samples by the Metrohm automated electrode method was modified between the September and November 1990 samples to reduce the difference between the value reported for the first sample and those reported in subsequent analyses. The method was modified by having two samples of de-ionized water analyzed before each series of samples was analyzed by the Metrohm automated electrode method. The purpose of the change was to extend the stabilizing period of the automated electrode after calibration.

A Grubb's test (Taylor 1987) identified several outliers:

- the first samples analyzed using the Metrohm automated electrode method from Maxwell Lake ($T_{(8)}$ =2.24), Stocking Lake ($T_{(8)}$ =2.00), and Old Wolf Lake ($T_{(8)}$ = 2.00) in November 1990 at a 5% risk of false rejection;
- the sixth 60-mL syringe sample analyzed using the Orion Ross combination pH electrode method from Maxwell Lake ($T_{(6)}$ =1.91) in August 1990 at a 3% risk of false rejection; and
- the fifth 1-L bottle sample analyzed using the Metrohm automated electrode method from Maxwell Lake ($T_{(6)}$ =1.83) in February 1990 at a 4 % risk of false rejection.

The first set of outliers indicate that the modification to the method of analysis using the Metrohm automated electrode method did not eliminate the bias on the first sample after calibration. Only one pH value analyzed using the Orion Ross combination pH electrode method was identified as an outlier.

The randomness of the variability in pH values reported by each analytical method was evaluated (Table 3, Figures 3 to 6). The pH values analyzed using the Orion Ross combination pH electrode method were normally distributed about the sample mean for ambient water from Old Wolf Lake (p=0.30), Maxwell Lake (p=0.55), and Stocking Lake (p=0.63). The influence of the fifth sample analyzed caused the distribution of water samples from Spectacle Lake (p=0.03) not to be normally distributed about the mean. The distribution of these values showed more reported values near the mean and tails than in the intermediate regions, and a pH value for the intermediate region that was greater than the mean of the distribution ("negatively skewed").

Values of pH reported for ambient water from Old Wolf Lake (p=0.354) and Spectacle Lake (p=0.646) analyzed using the Metrohm automated electrode method were normally distributed about the sample mean. The pH values for ambient water from Maxwell Lake ($p < 0.01$) and Stocking Lake (p=0.022) using the Metrohm automated electrode method were not normally distributed about the sample mean. This is attributed to the influence of the first sample analyzed. The characteristics of these latter distributions were similar to those observed using the Orion Ross combination pH electrode method for Spectacle lake.

The randomness of the variability in pH values reported, using the Metrohm automated electrode for 1-L bottle samples and the Orion Ross combination pH electrode for 1-L bottle samples and 60-mL syringe samples, was shown in Table 5 and Figures 7 and 8. The variability of pH values was normally distributed for all samples collected using:

- the 1-L bottle samples analyzed by the Orion Ross combination pH electrode method (p=0.813, p=0.98);
- the 60-mL syringe samples analyzed by the Orion Ross combination pH electrode method(p=0.680, p=0.22); and
- the 1-L bottle samples analyzed by Metrohm automated electrode method (p=0.202).

Only the samples collected in August and analyzed using the Metrohm automated electrode method were not normally distributed. A step decrease of 0.1 pH units in 1-L bottle samples was observed between samples 1, 2, 3 and samples 4, 5, 6.

4.4 Variability over Time

The pH values in the November 1990 ambient lake water samples were measured by the Metrohm automated electrode. Sample analyses were then immediately repeated to evaluate changes over time (Table 2). The mean pH values were lower (mean difference values ranged from 0.04 to 0.07 pH units) in the second series for all four lakes. The standard deviations either increased over time (in samples from Maxwell Lake and Stocking Lake) or were similar over time (in samples from Old Wolf Lake and Spectacle Lake).

Both series of samples analyzed were equal to or less than the U.S. EPA intralaboratory precision objective (the standard deviation $\leq$ 0.05 pH units).

The results of the *t-test* indicated that pH values were significantly different over time in samples collected at Maxwell Lake (p=0.0001), Stocking Lake (p=0.0001), Old Wolf Lake (p=0.0002), and Spectacle Lake (p=0.038).

5 CONCLUSIONS

Values for pH analyzed by the Orion Ross combination pH electrode method were higher than those analyzed by the Metrohm automated electrode method in 7 of 10 de-ionized water samples and in 42 of 47 ambient lake samples. The reported pH values for each method of analysis are *unique* because:

- the differences between the values were significant; and
- the LRTAP acid rain QC interlaboratory study's acceptable error between reported values of 0.25 was exceeded by one de-ionized sample (10% of the de-ionized water samples collected) and three samples (approximately 7% of the ambient lake samples collected) from four lakes.

Reported pH values using the Metrohm automated electrode method are considered *unreliable* because the data series contained outliers and the variability was high and not always random. The first sample analyzed contributed a significant amount to this variability. Increased variability in these samples is attributed to:

- the differences in ionic strengths between the low ionic strength lake samples and the ionic strengths of the calibration solutions;
- the stabilizing period before measuring pH values; and
- the calibration procedures of the electrode.

Reported values for pH from 1-liter bottle samples using both analytical methods changed over time.

Consistent trends were absent between pH values from the two sampling methods. The two sampling methods are considered *unique* because:

- the differences between pH values from 1-L bottle samples and 60-mL syringe samples were significant;
- the variability within analytical methods were different and exceeded the U.S. EPA intralaboratory precision objective values (standard deviation ≤ 0.05 pH units); and
- the acceptable error of 0.25 between values, set by the LRTAP acid rain QC interlaboratory study, was exceeded.

6 RECOMMENDATIONS

Ionic strength of ambient water quality samples determines the analytical procedure used to measure pH. We recommend that:

- the Orion Ross combination pH electrode method be used with the 60-mL syringe sampling method for data required to meet the LRTAP criterion for interlaboratory acceptable error values or the EPA intralaboratory precision objectives.

- the conductivity of ambient water quality samples should be used to indicate ionic strength. If the conductivity of ambient water quality samples is less than 1000 u S/cm, then the Orion Ross combination pH electrode method should be used. The Metrohm automated electrode should only be used for high ionic strength samples or when low ionic strength solutions have been used in the calibration procedure.

- water samples be analyzed for pH as soon as possible to minimize changes in pH values caused by gas exchange.

- reported values for pH using the two analytical methods be stored separately and evaluated separately.

- a data quality flag be associated with all values that were analyzed immediately after the Metrohm automated electrode was calibrated.

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TABLE 1: Comparison of pH values from analytical Methods for the Lake Trend Monitoring Program. Samples collected on September 21, 1990

Sample type	Samples analyzed immediately				Samples analyzed over time by the Orion Ross combination pH electrode method			
	Metohm automated electrode method	Orion Ross combination electrode method	Order of analyses for both methods	Differences between analytical methods	Order of analyses for both methods	Day 0	Day 3	Differences between analytical Days
PRE-MAXWELL	5.484	5.608	10	0.124	13	5.608	5.65	0.042
SAMPLE1 DAY1 POST OLD WOLF	5.517	5.622	6	0.105	12	5.622	5.61	0.012
SAMPLE1 DAY1 POST OLD WOLF	5.541	5.618	5	0.077	11	5.618	5.63	0.012
SAMPLE1 DAY1 POST OLD WOLF	5.704	5.604	4	0.1	10	5.604	5.62	0.016
SAMPLE1 DAY2 PRE MAXWELL LK.	5.472	5.59	9	0.118	9	5.59	5.62	0.03
SAMPLE1 DAY2 PRE MAXWELL LK.	5.531	5.602	8	0.071	8	5.602	5.66	0.058
SAMPLE1 DAY2 PRE MAXWELL LK.	5.497	5.63	7	0.133	7	5.63	5.65	0.02
SAMPLE1 DAY2 PRE MAXWELL LK.	5.593	5.648	3	0.055	6	5.648	5.65	0.002
SAMPLE1 DAY2 PRE MAXWELL LK.	5.706	5.646	2	0.06	5	5.646	5.66	0.014
SAMPLE1 DAY2 PRE MAXWELL LK.	6.268	5.645	1	0.623	4	5.645	5.65	0.005
Mean	5.6313	5.6213		0.147		5.62	5.64	0.021
Standard Deviation (A) (B)	0.239	0.021		0.170		0.021	0.018	0.017
Mean *	5.561			0.094				
Standard Deviation * (A) (B)	0.089			0.029				
Ambient lake samples								
Maxwell Lake	7.002	7.53	11	0.528	3	7.53	7.47	0.06
Stocking Lake	7.168	7.455	12	0.287	2	7.455	7.32	0.135
Spectacle Lake	7.175	7.39	13	0.215	1	7.39	7.39	0

* Mean and Standard Deviations calculations excluding sample value 6.268.
Grubb's test for outlying values(Taylor 1987) identified this value as an outlier (T(10)=2.665).

A. LRTAP L-24 acid rain QC interlaboratory study
use an acceptable error between reported values of 0.25 (Arafat and Aspila 1990).

B. EPA intralaboratory precision objective for pH measured in an analytical laboratory is a standard deviation of 0.05 pH units. (Silverstein et al 1987)

TABLE 2: Comparison of pH values from analytical methods for the Lake Trend Montoring Program. Samples collected on November 8, 1990

	1- L bottle samples analyzed Immediately				1-L bottle samples analyzed over time by the Metrohm automated electrode method			
Sample Type: Ambient lake water Descrete water sample Lake name	Metohm automated electrode method	Orion Ross combination electrode method	Order of analyses for both methods	Differences between analytical methods	Order of analyses for both methods	Run 1	Run 2	Differences between analytical Runs
	7.089	7.31	1	0.221	1	7.089	7.01	0.079
	7.18	7.36	2	0.18	2	7.18	7.105	0.075
Maxwell Lake	7.194	7.36	3	0.166	3	7.194	7.124	0.07
60-mL syringe sample analyzed	7.203	7.34	4	0.137	4	7.203	7.141	0.062
using the Orion Ross combination	7.208	7.32	5	0.112	5	7.208	7.149	0.059
electrode pH value: 7.35	7.225	7.33	6	0.105	6	7.225	7.158	0.067
	7.22	7.36	7	0.14	7	7.22	7.167	0.053
	7.229	7.34	8	0.111	8	7.229	7.167	0.062
Mean	7.19	7.34		0.15		7.19	7.13	0.07
Standard Deviation (A) (B)	0.045	0.019		0.040		0.045	0.052	0.009
	6.98	7.25	9	0.27	9	6.98	6.882	0.098
	7.025	7.2	10	0.175	10	7.025	6.958	0.067
Stocking Lake	7.06	7.21	11	0.15	11	7.06	6.977	0.083
60-mL syringe sample analyzed	7.056	7.22	12	0.164	12	7.056	7.001	0.055
using the Orion Ross combination	7.049	7.17	13	0.121	13	7.049	6.996	0.053
electrode pH value: 7.26	7.056	7.19	14	0.134	14	7.056	7.005	0.051
	7.061	7.2	15	0.139	15	7.061	6.998	0.063
	7.072	7.19	16	0.118	16	7.072	6.999	0.073
Mean	7.04	7.20		0.16		7.04	6.98	0.07
Standard Deviation (A) (B)	0.030	0.024		0.049		0.030	0.041	0.016
	6.708	6.93	17	0.222	17	6.708	6.677	0.031
	6.81	6.85	18	0.04	18	6.81	6.737	0.073
Old Wolf Lake	6.78	6.88	19	0.1	19	6.78	6.742	0.038
60-mL syringe sample analyzed	6.785	6.91	20	0.125	20	6.785	6.749	0.036
using the Orion Ross combination	6.839	6.91	21	0.071	21	6.839	6.784	0.055
electrode pH value: 6.92	6.806	6.86	22	0.054	22	6.806	6.796	0.01
	6.835	6.88	23	0.045	23	6.835	6.792	0.043
	6.853	6.88	24	0.027	24	6.853	6.801	0.052
Mean	6.80	6.8875		0.09		6.80	6.76	0.04
Standard Deviation (A) (B)	0.046	0.027		0.064		0.046	0.042	0.019
	7.055	7.3	25	0.245	25	7.055	7.008	0.047
	7.092	7.28	26	0.188	26	7.092	7.075	0.017
Spectacle Lake	7.103	7.31	27	0.207	27	7.103	7.094	0.009
60-mL syringe sample analyzed	7.137	7.29	28	0.153	28	7.137	7.11	0.027
using the Orion Ross combination	7.139	7.25	29	0.111	29	7.139	7.127	0.012
electrode pH value: 7.20	7.146	7.3	30	0.154	30	7.146	7.117	0.029
	7.148	7.3	31	0.152	31	7.148	7.061	0.087
	7.182	7.3	32	0.118	32	7.182	7.079	0.103
Mean	7.13	7.29		0.17		7.13	7.08	0.04
Standard Deviation (A) (B)	0.040	0.019		0.045		0.040	0.038	0.035

A. LRTAP L-24 acid rain QC interlaboratory study use an acceptable error between reported values of 0.25 (Arafat and Aspila 1990).

B. EPA intralaboratory precision objective for pH measured in an analytical laboratory is a standard deviation of 0.05 pH units. (Silverstein et al 1987)

TABLE 3: Comparison of the distribution in pH values from analytical methods fot the Lake Trend Monitoring Program.
Samples collected on September 21, 1990 and November 8, 1990

Sample Type: Ambient lake water Descrete water sample Lake name	**Metrohm automated electrode method 1-L bottle samples**	**Orion Ross combination electrode method 1-L bottle samples**
Maxwell Lake November,1990	Sample #1 reported a pH value approximating (Mean - (2*STD)) Kurtosis= 5.075 Skewness= - 2.143 Quantiles 10th 7.089 25th 7.184 Mean 7.194 Median 7.206 75th 7.224 90th 7.229	Sample #1 reported a pH value between (Mean - (STD)) and (Mean - (2*STD)) Kurtosis= -1.27: Skewness= - 0.319 Quantiles 10th 7.31 25th 7.323 Mean/ Median 7.34 75th/90th 7.36
Stocking Lake November,1990	Sample #1 reported a pH value approximating (Mean - (2*STD)) Kurtosis= 3.50 Skewness= - 1.858 Quantiles 10th 6.98 25th 7.031 Mean 7.089 Median 7.184 75th 7.061 90th 7.072	Sample #5 reported a pH value between (Mean - (STD)) and (Mean - (2*STD)) Kurtosis= 1.457 Skewness= 0.837 Quantiles 10th 7.17 25th 7.19 Mean/ Median 7.20 75th 7.218 90th 7.25
Old Wolf Lake November,1990	Sample #1 reported a pH value approximating (Mean - (2*STD)) Kurtosis= 1.914 Skewness= - 1.234 Quantiles 10th 6.708 25th 6.78 Mean 6.802 Median 6.808 75th 6.838 90th 6.853	Samples #1 and # 2 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)) and (Mean - (STD)) and (Mean - (2*STD)) Kurtosis= - 0.888 Skewness= 0.236 Quantiles 10th 6.85 25th 6.865 Mean/ Median 6.88 75th 6.91 90th 6.93
Spectacle Lake November,1990	Samples #1 and # 8 reported pH values between (Mean - (STD)) and (Mean -(2*STD)) and (Mean + (STD)) and (Mean +(2*STD)) Kurtosis= 0.166 Skewness= - 0.569 Quantiles 10th 7.055 25th 7.095 Mean 7.125 Median 7.138 75th 7.148 90th 7.182	Sample #5 reported a pH values approximating (Mean - (2*STD)) Sample #3 reported a pH values approximating (Mean - (STD)) Kurtosis= 3.404 Skewness= - 1.772 Quantiles 10th 7.25 25th 7.285 Mean 7.291 Mediar 7.3 75th 7.3 90th 7.31
De-ionzed water September, 1990	Sample #1 reported a pH value exceeding (Mean + (2*STD)) Kurtosis= 6.776 Skewness= 2.502 Quantiles 10th 5.473 25th 5.494 Median 5.536 Mean 5.631 75th 5.705 90th 6.212	Samples #1, #2, #3 reported pH values between (Mean - (STD)) and (Mean - (2*STD)) Sample #9 reported pH values between (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= - 1.375 Skewness= 0.042 Quantiles 10th 5.591 25th 5.604 Median/ Mean 5.62 75th 5.645 90th 5.648

TABLE 4: Comparison of pH values from analytical Methods for the Lake Trend Monitoring Program. Samples collected on February14, 1990 and August 2, 1990 from Maxwell Lake.

Samples collected on February 14, 1990							Samples collected on August 2, 1990						
Metrohm automated electrode method 1-L bottle sample	Orion Ross combination electrode method 1-L bottle sample	Orion Ross combination electrode method 60-mL syringe sample	Order of analyses for all methods	Difference between analytical results from the 60-mL syringe sample and Metrohm 1-L bottle sample	Orion Ross 1-L bottle sample	Difference between analytical results 1-L bottle sample	Metrohm automated electrode method 1-L bottle sample	Orion Ross combination electrode method 1-L bottle sample	Orion Ross combination electrode method 60-mL syringe sample	Order of analyses for all methods	Difference between analytical results from the 60-mL syringe sample and Metrohm 1-L bottle sample	Orion Ross 1-L bottle sample	Difference between analytical results 1-L bottle sample
6.961	7.08	7.16	1	0.199	0.080	0.119	7.6	7.39	7.37	1	0.23	0.02	0.21
6.973	7.12	7.12	2	0.147	0.000	0.147	7.6	7.4	7.37	2	0.23	0.03	0.2
7.011	7.09	7.14	3	0.129	0.050	0.079	7.6	7.44	7.42	3	0.18	0.02	0.16
7.006	7.11	7.1	4	0.094	0.010	0.104	7.5	7.41	7.34	4	0.16	0.07	0.09
7.079	7.09	7.12	5	0.041	0.030	0.011	7.5	7.42	7.35	5	0.15	0.07	0.08
6.977	7.1	7.11	6	0.133	0.010	0.123	7.5	7.36	7.23	6	0.27	0.13	0.14
7.00	7.10	7.13	Mean	0.12	0.03	0.10	7.55	7.40	7.35	Mean	0.20	0.06	0.15
0.043	0.015	0.022	Standard Deviation	0.053	0.030	0.048	0.055	0.027	0.063	Standard Deviation	0.047	0.043	0.054

A. LRTAP L-24 acid rain QC interlaboratory study
use an acceptable error between reported values of 0.25 (Arafat and Aspila 1990).

B. EPA intralaboratory precision objective for pH measured in an analytical laboratory is a standard deviation of 0.05 pH units. (Silverstein et al 1987)

TABLE 5: Comparison of the distribution in pH values from analytical methods fot the Lake Trend Monitoring Program.
Samples collected on February14, 1990 and August 2, 1990

Sample Type: Ambient lake water Descrete water sample Lake name	**Metrohm automated electrode method**	**Orion Ross combination electrode method**
1-L bottle sample Maxwell Lake February 14,1990	Sample #5 reported a pH value approximating (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 2.136 Skewness= 1.42 Quantiles 10th 25th Median Mean 75th 90th 6.96 6.97 6.991 7.001 7.01 7.079	Sample #2 reported a pH value approximating (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= -0.859 Skewness= 0.418 Quantiles 10th 25th Median Mean 75th 90th 7.08 7.09 7.095 7.098 7.11 7.12
60-mL syringe sample Maxwell Lake February 14,1990		Samples #1 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 0.068 Skewness= 0.795 Quantiles 10th 25th Mean/Median 75th 90th 7.10 7.11 7.12 7.14 7.16
1-L bottle sample Maxwell Lake August 2,1990	Kurtosis= - 3.33 Skewness= 0.00 Quantiles 10th 25th Mean/ Median 75th 90th 7.5 7.5 7.55 7.6 7.6	Samples #3 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 0.586 Skewness= - 0.435 Quantiles 10th 25th Mean Median 75th 90th 7.36 7.39 7.403 7.405 7.42 7.44
60-mL syringe sample Maxwell Lake August 2,1990		Samples #3 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)), Sample #6 reported a pH value between (Mean - (STD)) and (Mean - (2*STD)) Kurtosis= 3.02 Skewness= - 1.372 Quantiles 10th 25th Mean Median 75th 90th 7.23 7.34 7.35 7.36 7.37 7.42

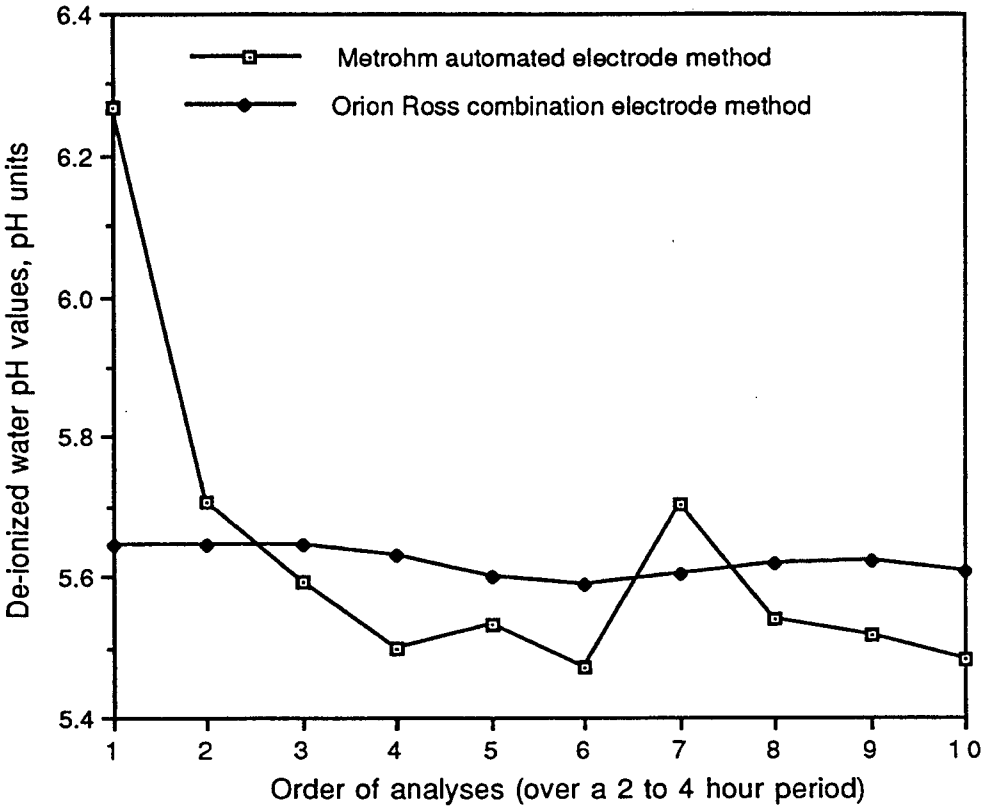

FIGURE 1: Comparison of pH values analyzed by two analytical procedures Samples collected September 21, 1990.

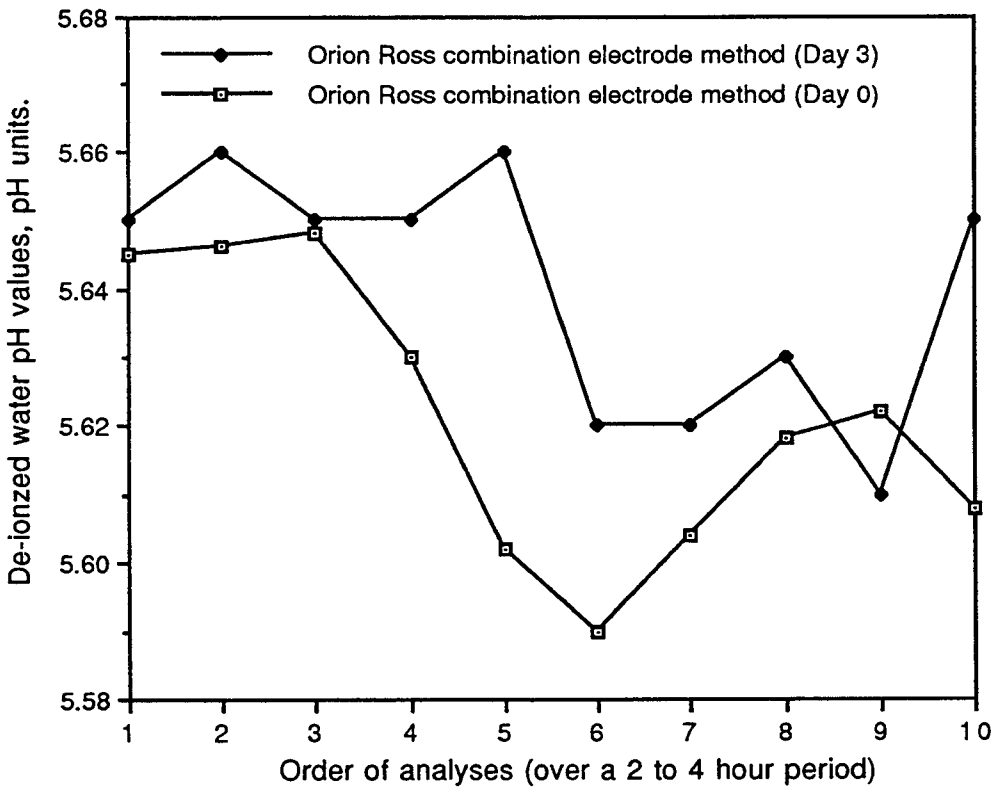

FIGURE 2: Comparison of pH values analyzed over time Samples collected September 21, 1990.

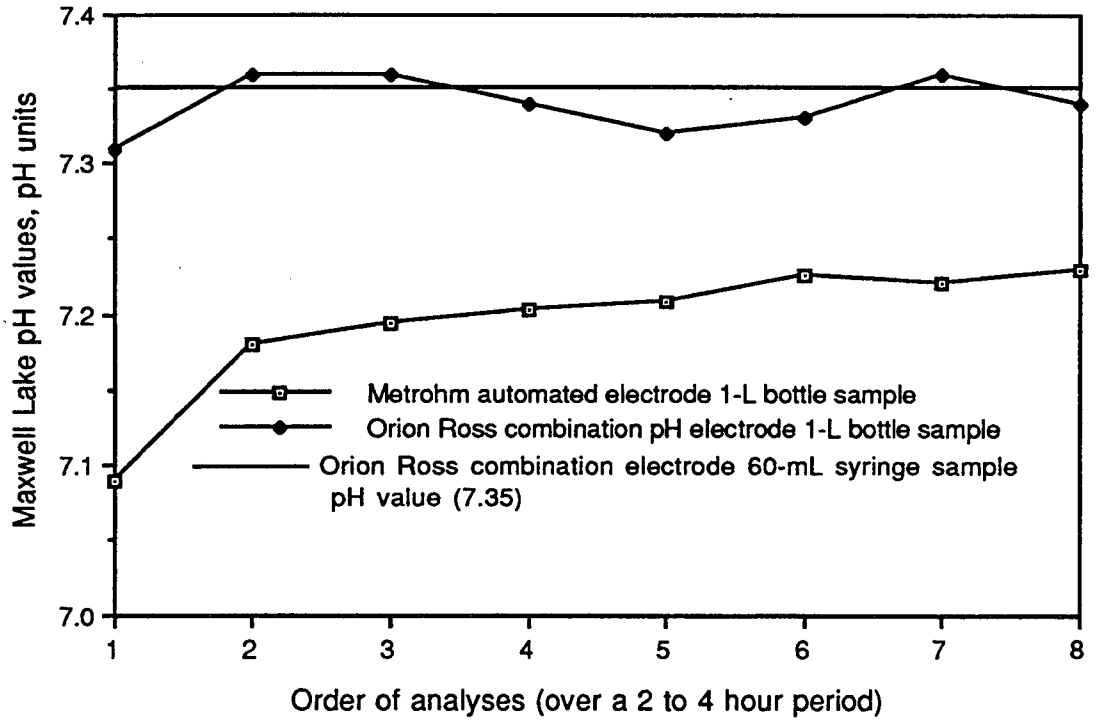

FIGURE 3: Comparison of pH values analyzed by two analytical methods and two sampling methods for Maxwell Lake samples, November 8, 1990.

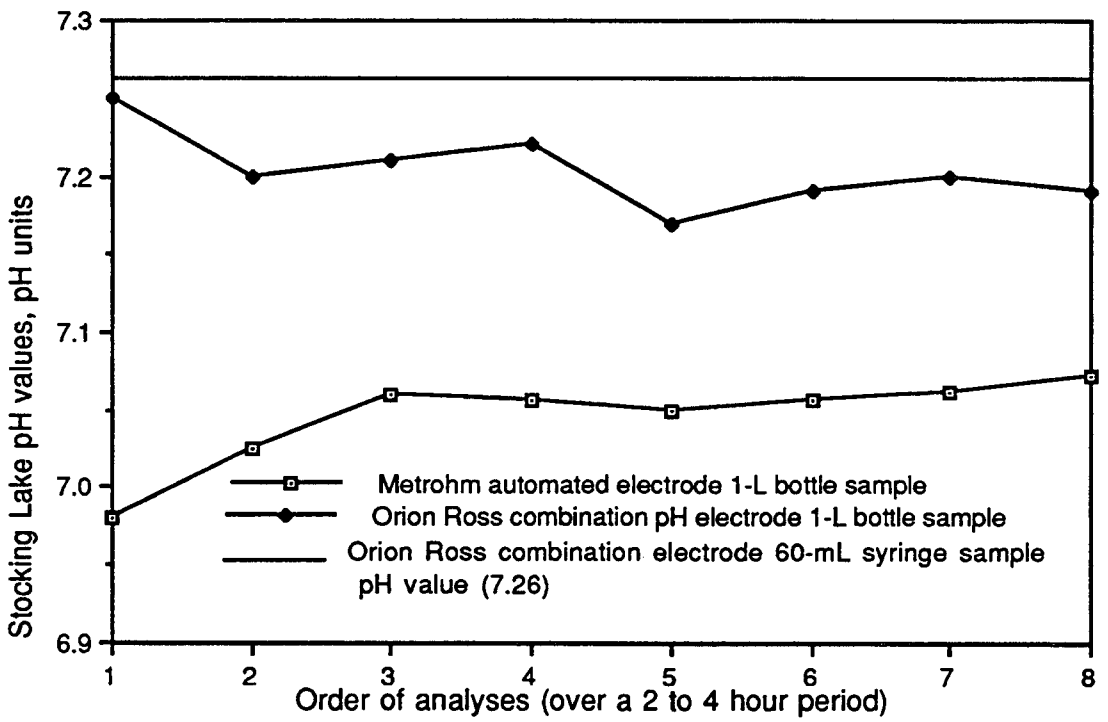

FIGURE 4: Comparison of pH values analyzed by two analytical methods and two sampling methods for Stocking Lake samples, November 8,1990.

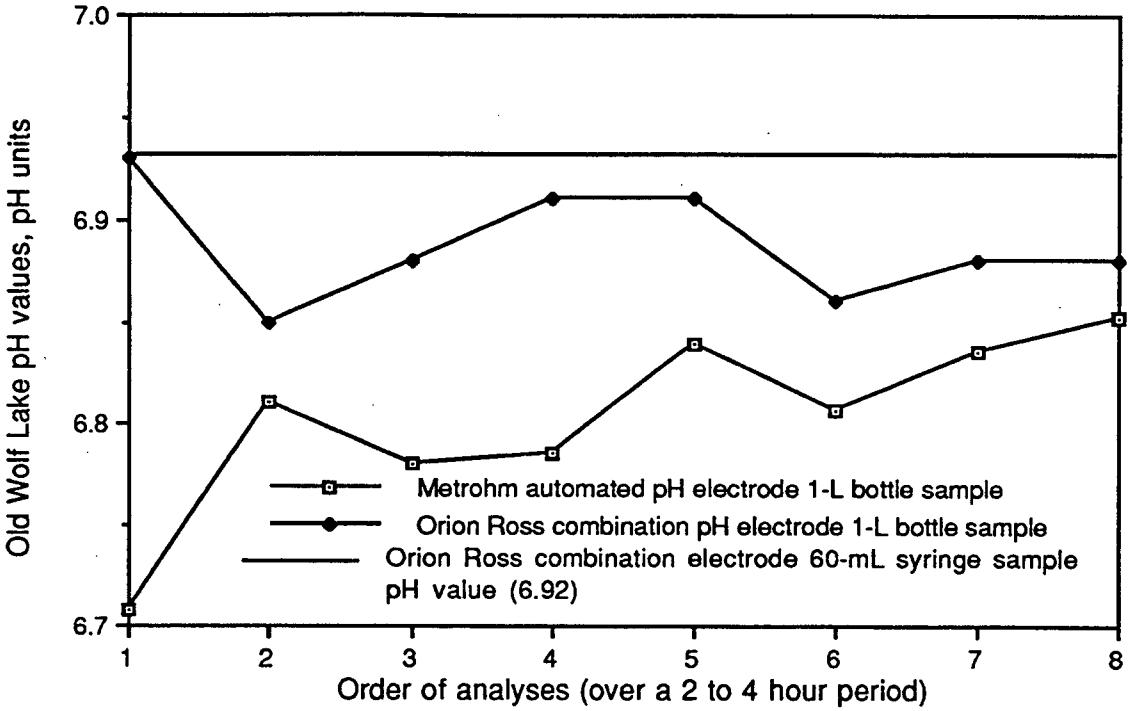

FIGURE 5: Comparison of pH values analyzed by two analytical methods and two sampling methods for Old Wolf Lake samples, November 8, 1990.

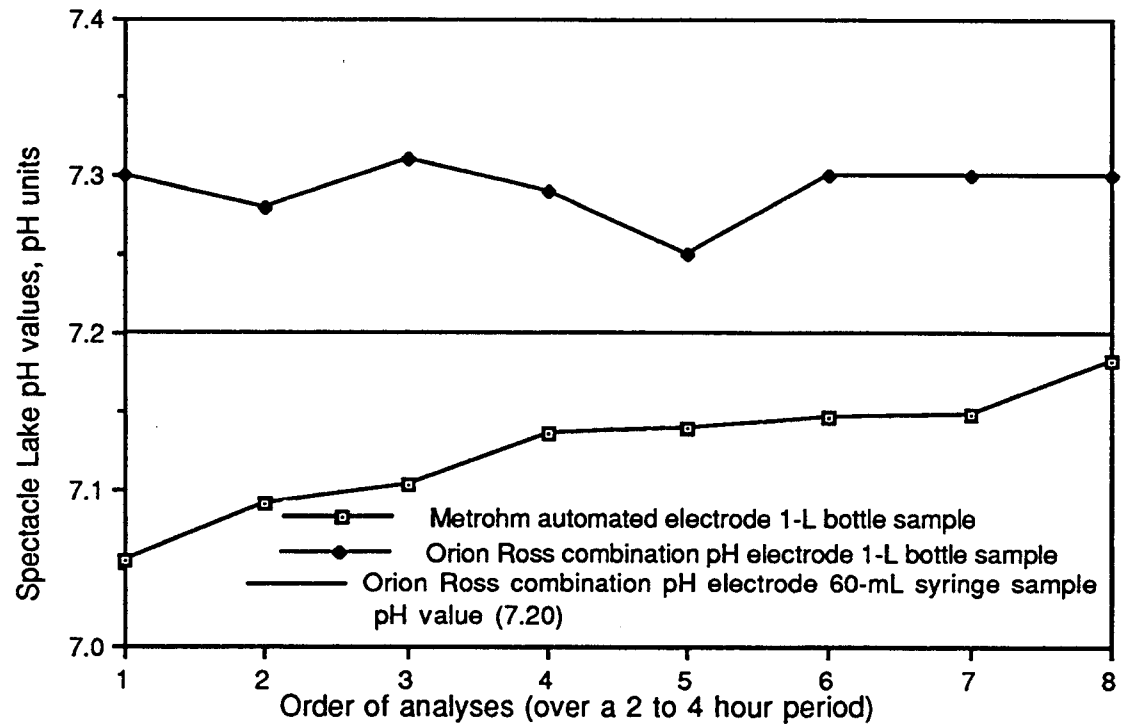

FIGURE 6: Comparison of pH values analyzed by two analytical methods and two sampling methods for Spectacle Lake samples, November 8, 1990.

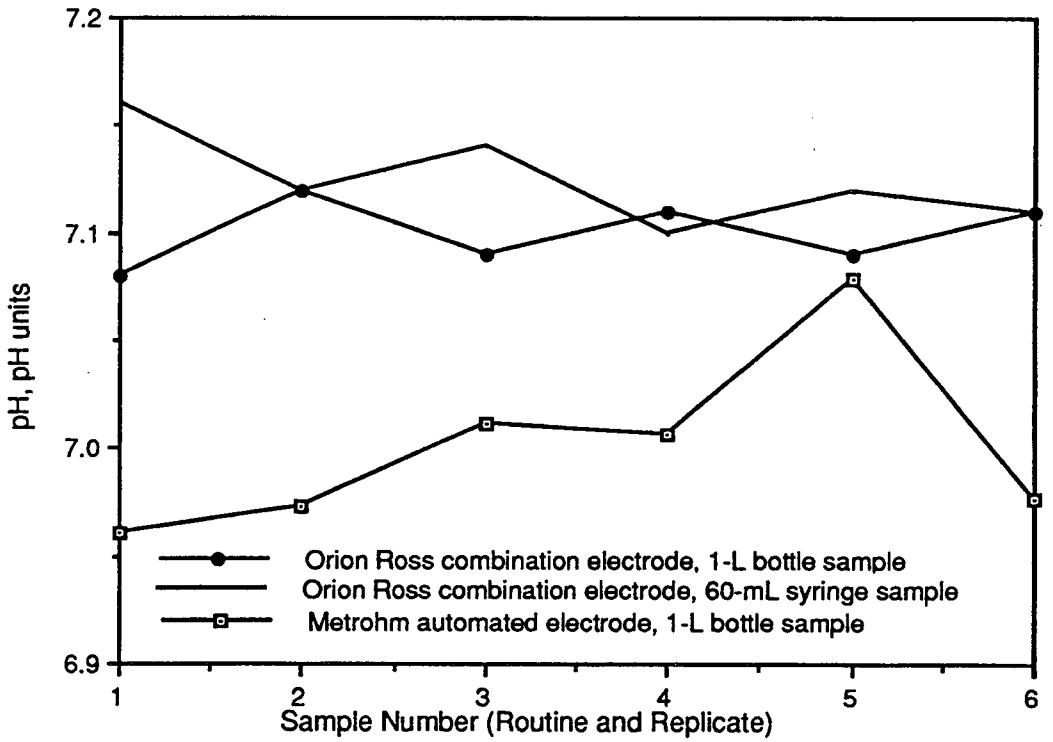

Figure 7: Values for pH reported for two sampling methods and analyzed using the Metrohm automated electrode and the Orion Ross combination electrode Sample date February 14,1990, Maxwell Lake

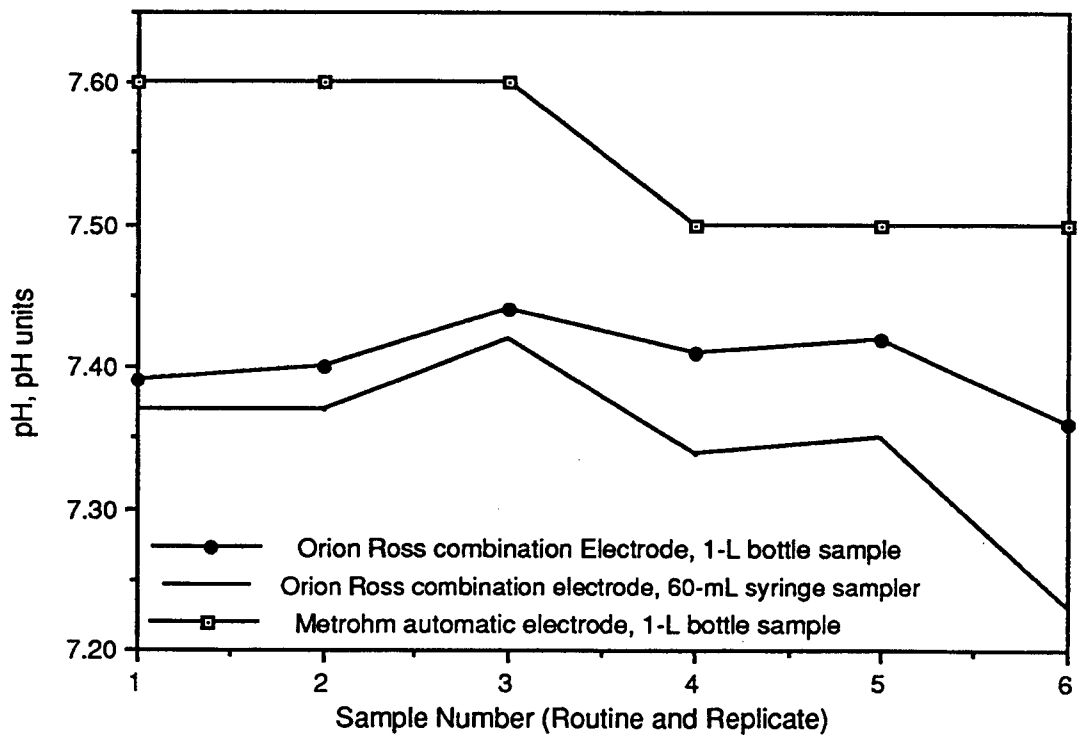

Figure 8: Values for pH reported for two sampling methods using the Metrohm automated electrode and the Orion Ross combination electrode Sample date August 2, 1990, Maxwell Lake

PROTOCOLS FOR WATER QUALITY SAMPLING THROUGH ICE

by

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Introduction

The Water Quality Monitoring Network in the Pacific and Yukon region is comprised of 58 stations located on rivers of federal interest. Nineteen of these stations are designated as Federal, 18 are Federal-Provincial (operated under an Agreement with the Province of B.C.), and 21 are Federal-Territorial (operated under an Agreement with the Department of Indian Affairs and Northern Development).

Samples at most of the sites are collected on a routine basis (weekly, bi-weekly or monthly). The data is primarily being collected to assess long term changes in water quality - ie. trend assessment - but is also used for a variety of other purposes (general surveillance, baseline data, water quality objectives, emerging issues, etc.).

Variables sampled under the program include immediates, major ions, nutrients, physical variables, and a suite of total trace metals. The water quality sampling kits used contain a variety of bottles of different sizes and materials which are specific to the variables in question. For open water sampling, a multiple sampler which holds all of these various bottles is used. During winter, if the rivers stay open (or the ice is thin enough to break through) the multiple sampler can still be used. At our sites in Northern B.C. and the Yukon however, the ice is usually too thick to use the regular procedure, and through-ice sampling techniques must be employed.

Summary of Through-Ice Sampling Procedures

The though-ice sampler consists of a 2 meter long plastic tube, approximately 4 cm in diameter. At one end of the tube is a t-bar handle (made of the same tubing): at the opposite end is a plastic holder which accomodates a 2 litre polyethylene bottle. A length of rubber tubing attached to the shaft of the sampler holds the bottle in place during sampling. A No. 27 polyethylene stopper attached to a cord is used to plug the bottle opening until it is well below the ice surface and away from potential contamination. (See Figure 1.)

The 2 litre bottle is lowered through a drill hole via the through-ice sampler, and sample water collected from well below the lower ice surface. During routine sample collection, two 2 litre bottles are filled with sample water in this manner. This water is then used to fill all of the kit bottles used for the different variables. One of the 2 litre bottles is acid-washed, and used to fill bottles for the metals variables. The other is "regularly" washed (phosphate-free soap), and used to fill all of the other variables bottles (those for immediates, major ions, nutrients, and physical variables).

As in our protocols for open water sampling, the through-ice sampling protocols stress the importance of minimizing the possibility of sample contamination. Keeping the area around the drill hole clean, allowing time for potential contaminants to be flushed away from the hole before sampling, and exposing sampling and kit bottles (both prior to and after sampling) to the open air as little as possible are some of the main considerations. These and other QA aspects to be considered are outlined in greater detail in the formal "Sampling Through Ice" Protocol found in the next section.

Figure 1. Through-Ice Sampler

SAMPLING THROUGH ICE PROTOCOLS

Andrea L. Ryan

Environment Canada

Pacific and Yukon Region

"Sampling Through Ice" Protocol

Category: Field Sampling [FS000004.PR1]

Subject: SAMPLING THROUGH ICE

Effective Date: 01 September 1993

Protocol:

(1) Always proceed with caution over ice and do not jeopardize your safety. Check the ice for safety and thickness with a rod or ice chisel every few steps. Ice over moving water can be of varying thicknesses, and the strength of the ice cannot be estimated from the apparent thickness near the shore. Be aware that ice downstream of bridge supports may be thin as a result of modified flow patterns and de-icing agents. Honeycombed ice and areas over rapids should be avoided. Always have someone accompany you, and carry a length of rope to use as a life line. If the ice is unsafe, do not take a sample. Never take unnecessary risks.

(2) In preparation for measuring air temperature, remove cover from field thermometer and place the thermometer in the shade, preferably about 1 metre above the ground and away from any vehicle, to minimize the heat influence from anything other than ambient air temperature. Leave the thermometer for 5 - 10 minutes or for the time it takes to collect the water samples. Measure the air temperature to the nearest 0.5 degrees (°C), and record the value in its designated location on the data card.

(3) Winter sampling location should be as close as possible to the location indicated on the site map. If sampling near a bridge, the site should be far enough upstream to avoid contamination from road salt. The site should be chosen where the water is known to be deep to avoid stirring up bottom sediments and to ensure that there is water flowing under the ice at your selected spot. It is preferable to select a site where the ice is sagging rather than bulging. The sampling location used should be recorded in the "Remarks" section of the data card.

(4) Clear loose ice and snow from sampling location, and drill through ice with auger. Keep area around hole clean and free of potential contamination (dirt from drill, boots, etc.).

(5) Remove all ice chips and slush from hole, using a plastic sieve. Wait several minutes for the water to flow freely under the ice, allowing potential contaminants to clear.

(6) Load a clean 2 litre bottle marked AW (acid washed) into the through-ice sampler. Remove the bottle cap, and insert stopper with attached cord into the bottle opening. Lower the sampler and bottle through the hole until it is clear of the bottom of the ice surface, and into freely moving water. Remove the stopper by pulling the cord, and allow the bottle to fill. For the bottle to fill in fast flowing water the sampler may have to be held at different angles. Bring bottle back up and replace the cap (do not rinse).

(7) Repeat procedure outlined above, this time using the other clean 2 litre bottle marked **Reg** (normal wash).

(8) When both 2 litre bottles have been filled with sample, return to vehicle. If in-situ pH and conductivity are to be measured, refer to Protocols FS000012 and FS000013.

(9) From the 2 litre bottle marked **Reg**, fill the bottles in the kit that have red, green, yellow, white, and pink labels (ie. all bottles except those with blue labels). Swirl the bottle periodically during this procedure to ensure the sample remains well-mixed.

N.B.- Do not fill bottles with the RED labels from the 2 litre bottle marked AW. This 2 litre bottle has been washed with nitric acid and could contaminate the sample in the 100 ml bottles with red labels, which are analyzed for nitrogen compounds.

(10) From the 2 litre bottle marked AW, fill the bottles in the kit that have blue labels (ie. Teflon bottle for Mercury, 500 ml polyethylene bottle for metals, and 100 ml polyethylene bottle for Arsenic and Selenium).

(11) Record air temperature and place thermometer in sample bottle labelled "FIELD" to equilibrate for at least 3 minutes.

(12) Using the plastic gloves provided, add preservatives to those samples which need preservation, being sure to match each preservative with its similarly labelled sample bottle. Re-cap bottles tightly, and shake those to which preservatives have been added.

NOTE: Vehicle exhaust and cigarette smoke will contaminate water samples - these should be avoided when bottles are open.

(13) Measure the water temperature within 5 minutes of sampling. Read water temperature by holding the bottle and the thermometer at eye level, and keeping the bulb of the thermometer submerged in the sample. Record water temperature in appropriate spot on data card.

(14) Re-pack sampling kit, ensuring that glass bottles are separated from one another by plastic bottles to prevent breakage. Pack sponges in as tightly as possible to avoid bottle movement.

(15) Complete data card as per Protocol FS-17. Make a note in the "Remarks" section that the sample was collected through the ice. Put data card back in its plastic bag, and pack it into the sampling kit, along with the empty preservative vials.

(16) Do not allow samples to freeze.

(17) Send sampling kit back to the Conservation and Protection (C&P) Laboratories on the same day that the samples are collected.

NOTE: Any deviations from this protocol must be noted in the "Remarks" section of the data card.

Sampling Techniques:

- If sampling kit cannot be sent to the lab on day of sampling, bottles should be refrigerated overnight, and sent off the next day.
- If regular sample is taken from a bridge and river ice is thin, a hole of sufficient size to collect a sample (ie. with the regular multiple sampler) may be broken by dropping a weight attached to a hand line.
- If a bottle or cap is suspected of having been contaminated, rinse it thoroughly with river water, and make a note on the data card.

Operational Responsibility:

1. Sample Collector
2. Area Manager
3. Head, Operations Division
4. Head, Networks Division

Modification Approval and Justification:

01 September 1993 Amended to reflect use of clean acid washed and normally washed 2 litre bottles.

QUALITY ASSURANCE FOR ELECTRONICALLY ACQUIRED DATA

Norman L. Wade

Environment Canada

Pacific and Yukon Region

WATER RESOURCES BULLETIN
VOL. 29, NO. 2 AMERICAN WATER RESOURCES ASSOCIATION APRIL 1993

QUALITY ASSURANCE TECHNIQUES FOR ELECTRONIC DATA ACQUISITION[1]

Paul H. Whitfield and Norman L. Wade[2]

ABSTRACT: Electronic instruments are increasingly being used to gather water quality data. Quality assurance protocols are needed which provide adequate documentation of the procedures followed in calibration, collection, and validation of electronically acquired data. The level of precision of many data loggers exceeds the technology which is commonly used to make field measurements. Overcoming this problem involves using laboratory quality equipment in the field or enhanced quality control at the time of instrument servicing. Time control procedures for data loggers are needed to allow direct comparisons of data between instruments. Electronic instruments provide a mechanism to study transient events in great detail, but, without time controls, multiple loggers produce data which contain artifacts due to timing errors. Individual sensors deployed with data loggers are subject to different degrees of drift over time. Certain measurements can be measured with defined precision and accuracy for long periods of time, while other sensors are subject to loss of both precision and accuracy with increasing time of use. Adequate quality assurance requires the levels of precision and accuracy be documented, particularly those which vary with increasing time deployment.
(KEY TERMS: water quality; quality assurance; electronic acquisition; continuous monitoring; data logging.)

INTRODUCTION

Quality assurance of electronically acquired data is a new challenge in the water quality field. The use of data loggers capable of frequent, high precision measurements of water quality variables offers many opportunities for enhanced data collection. Ensuring that electronically acquired data are of known quality involves adapting standard quality assurance techniques to new applications. Many applications challenge the limits of our current methods. The development of adequate quality assurance protocols for data loggers also includes data and method validation, and standardization of measurement techniques. Some of the approaches being developed in our programs are described.

Environment Canada operates two electronic data gathering sites in the Lower Fraser Valley of British Columbia to allow the assessment of the effects of precipitation on water quality conditions in small streams (Whitfield *et al.*, 1993; Dalley, 1986) and other transient events (Whitfield and Wade, 1992). This project has as a general goal the development and application of instrumentation and procedures to allow water quality data to be gathered in an effective and efficient manner. In support of this goal, instrumentation is being tested and evaluated, particularly with respect to quality assurance questions such as the length of deployment between servicing. The sites are located on Kanaka Creek and on the Serpentine River; two small streams in the Greater Vancouver area.

Through hands-on experience with operating electronic data stations, we have experienced many situations for which standard procedures did not exist. These include, but are not limited to, the quality assurance of sensors, hardware, software, and data standards. Obtaining valid data from sensors requires new procedures for verification that are field serviceable and of appropriate precision and accuracy. Existing field methods are insufficient relative to the accuracy obtainable with electronic sensors. There is also a need for quality assurance protocols to be compatible with other agencies and other data loggers, since other agencies may collect similar, but not compatible, types of data.

To illustrate the importance of quality assurance procedures for electronic data acquisition procedures currently in use, we will highlight three specific areas: (1) sensor validations in the field, (2) time controls for data loggers, and (3) precision and accuracy of sensors over time.

[1]Paper No. 93007 of the *Water Resources Bulletin*. **Discussions are open until December 1, 1993.**
[2]Respectively, Head, Environmental Networks, and Senior Networks Technologist, Environmental Surveys Branch, 224 West Esplanade, North Vancouver, British Columbia V7M 3H7, Canada.

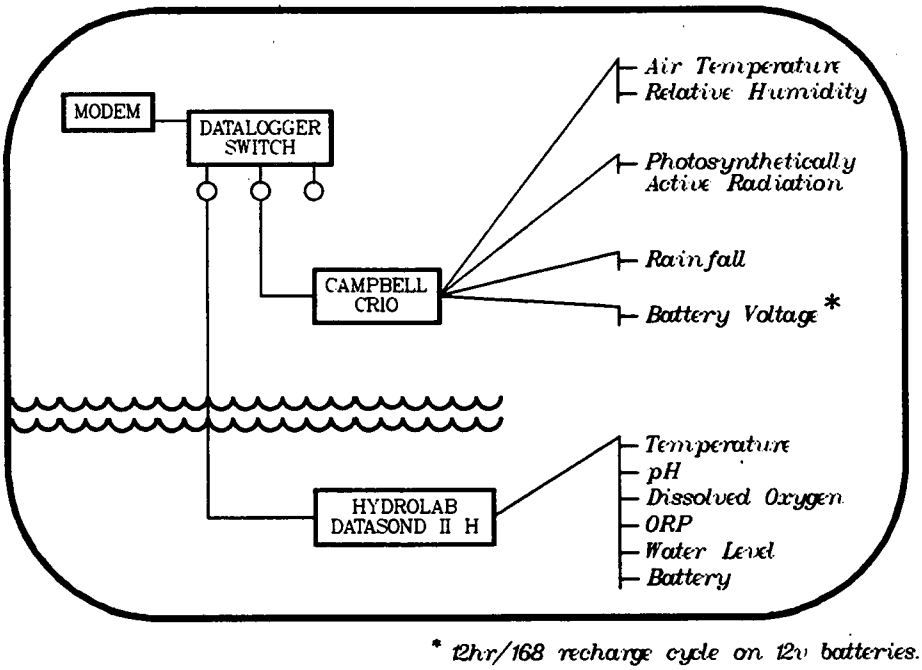

Figure 1. Schematic Diagram of Stations.

METHODS

The two electronic data acquisition stations are essentially identical in configuration. In-stream measurements of temperature, specific conductance, pH, dissolved oxygen, depth, and oxidation reduction potential [ORP] are made and logged with a Hydrolab Datasond IIH. The Hydrolab unit provides high resolution measurement of these variables: pH – low ionic strength (0.01 unit), specific conductance (0.01mS/cm), temperature (0.01°C), dissolved oxygen (0.01mg/l), oxidation reduction potential (ORP)(1mV), and depth (0.1m). [Values in parentheses are the manufacturers' stated resolutions.] Specific conductance, pH, and dissolved oxygen measurements are automatically compensated for temperature. Each site is also equipped with a Campbell Scientific CR10 Data Logger equipped with sensors for measurements of air temperature, relative humidity, photosynthetically active radiation [P.A.R.] and rainfall. These sensors are deployed in accordance with Atmospheric Environment Service (1989) protocols; temperature and humidity sensors are mounted in a Stephenson Screen enclosure, standard tipping bucket rain gauges are used, and P.A.R. sensors are mounted >2m above the surface. At each station, the two loggers are accessed through telephone lines, to a modem and data logger switch. The data logger switch also provides password security against intrusion. The station arrangement is shown schematically in Figure 1. Data is retrieved over phone lines at seven to ten day intervals.

Over the past two calendar years, these two stations have been fully operational close to 100 percent of the time. During 1989 the instream portion of the Kanaka Creek station was out of operation for a ten-day period due to severe flooding. With that one exception, all four loggers have been maintained in constant operation for two years, with occasional sensor failure.

QUALITY ASSURANCE

Quality assurance of electronically acquired data is a critical part of ensuring that the data so collected have value beyond local application. Protocols are developed so that the data being collected achieves the goal of good data which is well documented. The development of these protocols has required a broader view, since many other agencies collect similar, but not identical, data. In British Columbia for example, other agencies operating electronic data acquisition stations include: BC Ministry of Environment, Lands, and Parks, BC Ministry of Forests, Atmospheric Environment Service (Environment Canada), B.C. Hydro, and others. Data from each of the instruments

could be interchanged with other agencies if quality control procedures ensured compatibility. Each agency currently operates under a loose set of guidelines, data being gathered to meet specific goals and objectives. No common protocols exist at present, beyond the A.E.S. sensor siting guidelines. Common protocols for sensor calibration, hardware installation, software documentation, or data formats, while needed, do not exist at present.

Quality assurance includes both generic, and instrument or sensor specific issues. Our quality assurance concerns have been focused on the following issues:

1. Procedures are needed to allow validation of measurement techniques in different types of loggers. Water Quality loggers, such as the Hydrolab instruments we use, are off the shelf and simple to use but they are considerably less flexible than the programmable generic loggers. To maintain adequate quality assurance, it is crucial that both types of loggers generate compatible data. Often this includes using the measurement techniques of off-the-shelf instruments for programmable loggers.
2. Conducting cross-comparison experiments between paired loggers and paired sensors provides information which indicates whether or not there is any instrument or sensor specific effects. The results from such experiments provide indications of sensor or instrument biases which could, should they exist, seriously compromise the validity of the data.
3. Water quality sensors are not as robust as some meteorological sensors, and require more frequent servicing. Optimized service schedules need to balance adequate data quality with frequency of servicing. We have been experimenting with extended instrument deployments to determine how long an instrument can be in operation before serious biases are introduced.
4. Procedures are needed to determine the validity of the data being gathered. This includes developing field procedures that allow the verification of the highly precise measurements possible with many data loggers. This requires enhancing field methods beyond their existing capacity or alternate solutions.
5. Data comparability and compatibility, particularly of data from different loggers, requires some degree of standardization. Implementation of this is sometimes difficult in the broad sense as many water quality data loggers are off the shelf, and use measurement techniques which are transparent to the users. The techniques used need to be fully documented for future reference. Inter-agency cooperation is needed so that data from different loggers and collected by different agencies can be compared.

Quality assurance is an active process of using procedures which provide the checks and balances necessary to provide good data. This is an area where a lot of work remains to be done. In our own work, we continue to find that simple mistakes have a large impact on the quality of the data. Spittlehouse (1989) notes that almost all of the problems encountered in data logger use are the result of operator error or sensor damage. So long as the data logger is protected from extreme environmental conditions, there is little risk of data logger failure. This clearly put the onus on the operators of data loggers to take all the steps necessary to ensure proper operation of the equipment.

The results from some of our early work on quality assurance for data loggers highlight three of the many quality assurance areas that merit consideration. First, the problems of field verification are identified. This is an area where much effort will continue to be needed. Second is the subject of time controls. The results of some experiments are presented. And lastly, the relationship between sensor precision and accuracy is discussed in relation to service schedules.

Field Verification

Sensor calibrations can change over time. This is especially true of water quality sensors which can be affected by fouling, breakage, and electrolytic drift. A procedure for field verification is necessary to verify that sensors are providing correct data. There are considerable practical limits to the precision with which a field data logger, which is capable of highly precise measurements, can be verified. It is extremely difficult to achieve the same degree of resolution of a data logger in the field using field instruments. In general, field instruments are very much less precise than are laboratory instruments, and are inadequate for verifying data loggers. Field verification techniques need to be as precise as laboratory techniques and as robust as field instruments. At the present time, such technology is not available.

Field verification should be performed using independent technology. Verification of electronic temperature sensors can be performed using a high precision mercury thermometer. Other measurements are often less suited to independent measurements. This is particularly true of 'electronic' measures such as pH and ORP (Eh) which are defined properties. Wet samples taken in the field can be used as a later stage validation, and form an important part of the quality assurance program. However, such samples are susceptible to drift and change over time. In addition, the delays associated with wet analysis of samples prevent the results from being used as an effective alternative to

on-site verifications. On-site calibration is in the same manner difficult to implement.

SITE LOG - DATA LOGGER ACCESS RECORD

Location:_____

Date:_____ Time:_____ Who:_____

Datasond #__ Type _____

Clock Time verified:_____ Adjusted:_____

Current Readings:

Time:_____

Temperature:_____

pH:_____

Conductance:_____

Dissolved Oxygen:_____

ORP:_____

Depth:_____

Battery:_____

Datafile Name:_____

Campbell CR10 #___ Who:_____

Clock Time verified:_____ Adjusted:_____

Current Readings: Time:_____

1._____	6._____	11._____	16._____
2._____	7._____	12._____	17._____
3._____	8._____	13._____	18._____
4._____	9._____	14._____	19._____
5._____	10._____	15._____	20._____

Datafile Name:_____

M&A-WQB-90/12

Figure 2. Example of the Loggers Access Records That are Maintained.

To overcome these problems, and to develop practical quality assurance for the sensors attached to data loggers, we operate our sensors for a prescribed period of time. Each 90-day duty cycle begins and ends with a complete calibration by an independent service company. The service report documents the degree of drift which has occurred, and an appropriate correction factor can then be applied to the data. Independent service of the sensors is an important part of the duty cycle. To operate in this manner means that an enhanced level of service from the company servicing the sensors is required. When the instrument is serviced, detailed records of alterations and changes are required to ensure that the instrument is fully functional. We inform the service company of the need for this level of documentation. These service records provide information essential to the service cycle of each individual sensor array. The service company is charged with the responsibility of ensuring that the electronics and sensors are fully operational and accurate. Isolating the operational responsibility for station operation from instrument servicing provides each facet with independent service goals. The result is a clear focus on good data being logged.

The production of good data requires a high standard of both servicing and record keeping. It is not always possible to evaluate and analyze the data when it is recovered from the data loggers. We maintain a paper trail of each interaction with the data loggers. Each time we interrogate the instrument, we record specific information which is used as a permanent record of the contact with the data logger and any recorded information. Maintaining this type of record is an essential quality assurance step of every data collection program. An example of our log sheet is given in Figure 2. While this sheet is specific to our programs, it does contain the elements which are essential to all programs. Included on the log form is a record of the most recent values. Recording the most recent values in this manner provides an immediate check for sensor failure. It is also possible to use this as a reference check when one of the sensors starts to fail. Maintaining accurate records of interactions with the data loggers is a fundamental principle of good quality assurance.

Time Controls

One of the first items we encountered as we initiated quality assurance experiments was the importance of time controls. Two instruments were deployed side by side to examine signal bias between a newly calibrated instrument and one which had been deployed for a period of time. Figure 3 illustrates typical pH and specific conductance results from the experiment when strict time controls were not being kept. When such results are first encountered, the impression is that one of the two instruments has failed. Plotting the response of one sensor unit against the response of the other sensor unit illustrates the results when sensors are operated without time control. Linking the data points in sequence, such as in Figure 3a&c (pH and specific conductance), show looping structures that result from two sensors sampling the same process (Figures 3b&d) at different times. This type of result typically is found when there is a rapid rate of change in the variable being measured by the two instruments, and there is a time discrepancy between the two instruments. Figure 4 illustrates the same comparison on the same instruments with clock correction in place. When the events being measured are highly transient and no local smoothing is being performed [i.e., no averaging], strict time controls

Serpentine River

July 5-12, 1990

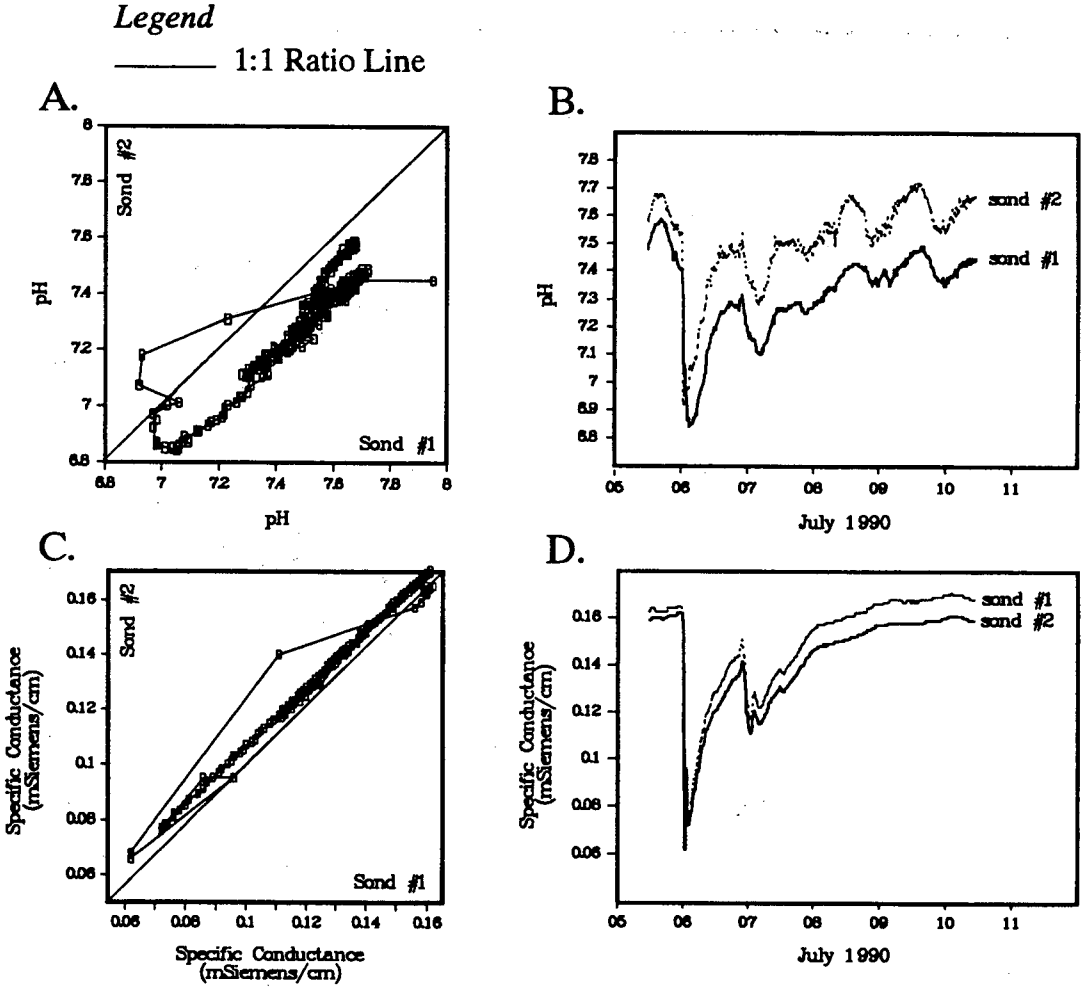

Figure 3. Data Relationship Without Time Control: A. pH vs pH; B. 2 pH Sensors Over Time; C. Conductance vs Conductance; D. Conductance Sensors Over Time.

have been identified as being necessary. In this example, we considered only the paired instruments. It is, however, an important quality control protocol to ensure that such artifacts are not generated between any pair of instruments. To avoid the potential for time artifact generation, we have adopted a strict time control system. In the time system used by our counterparts in the weather observation field, all clocks are maintained within ±30 seconds. Local clocks are adjusted to a tolerance of ±5 seconds, and records of adjustments are kept of all such corrections for future reference. Our data loggers and the computers used to interface with them, are maintained on UCT (Universal Coordinated Time). Weekly verification of local clocks is performed using the Time Clock at WWV (Fort Collins, Colorado). Records of time deviations are kept as part of the audit trail for the data loggers.

These procedures, although arbitrary, provide a degree of control on this critical aspect of high frequency data collection. These procedures are most critical when the system under study is subject to

Serpentine River

July 12-19, 1990

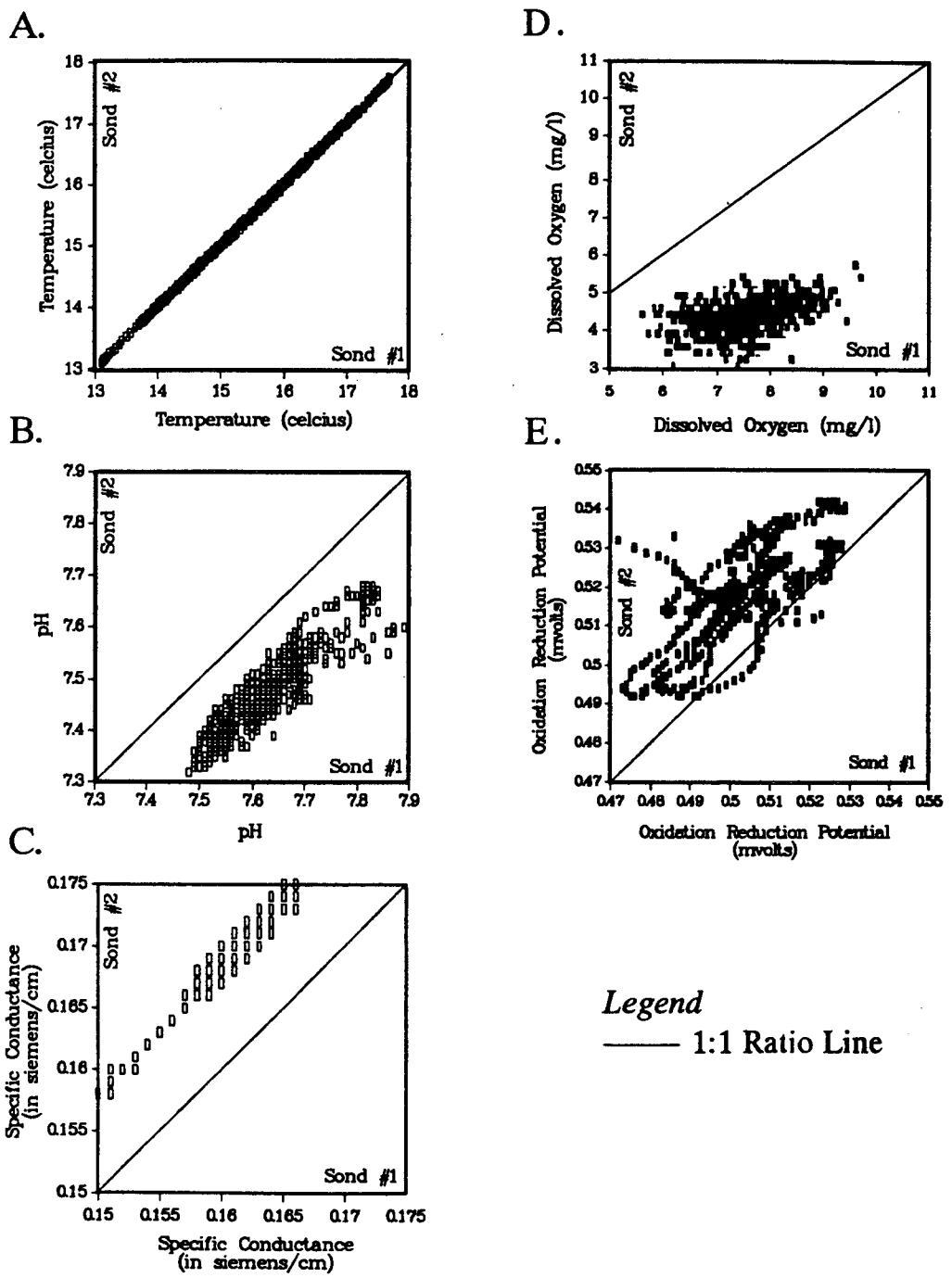

Figure 4. Bias Between Sensors of Long Deployed Sensors (Sond#2) and Newly Calibrated Sensors (Sond#1): A. Temperature; B. pH; C. Specific Conductance; D. Dissolved Oxygen; and E. Oxidation Reduction Potential.

rapid changes (Whitfield and Dalley, 1987; Whitfield and Wade, 1992). Increased sampling frequency may be an alternate solution in some cases, but memory capacity can quickly become strained when too high a frequency is maintained.

Maintenance of clocks in this manner requires considerable effort. For independent loggers, the need for such rigorous time control may not be necessary. If, on the other hand, where data collection programs require multiple loggers and or multiple sites for comparison, it will be necessary for procedures of this type to be implemented. We recommend that all data loggers have some documented degree of time control/verification as part of standard operating procedures.

Precision and Accuracy

The duration of time in service of the instruments is dependent upon several factors. Each instrument and sensor has its own time dependent behaviour. In particular, sensor drift varies between sensors and electrode type. We have performed a number of experiments to examine how much drift/bias is introduced into the data set over extended periods of deployment. For water quality variables, we find that dissolved oxygen sensors are the most susceptible to degradation in performance; ORP (Eh) and pH are subject to bias over time rather than decreased performance. Figure 4 compares the recording from a newly conditioned set of sensors (SOND#1) to one which had been in service for one year (SOND#2). The results for temperature show that both instruments produce the same result (Figure 4a). The results for pH and Specific Conductance and ORP show some bias. This bias is approximately +10 μSiemens for Conductance, 0.15 units low for pH, and 0.02 mVolts for ORP. Specific Conductance and pH sensors show a linear response to stream fluctuations, i.e., the amount of response is about the same for both the 'new' and 'old' instruments. In terms of a linear regression, there is a change in the intercept. Dissolved oxygen and oxidation reduction potential electrodes suffer decreased performance in two ways. The readings from the 'old' instrument have a significant low bias, and the 'old' instrument has a much slower response to stream changes. This is effectively a change in both the slope and the intercept of a regression. While the response changes were quite small for other types of electrodes, dissolved oxygen was severely impacted by the long deployment. However, it is interesting to note that, even after a year in service, the dissolved oxygen electrode still responded to fluctuations in stream oxygen levels. Knowing the original calibrations to real values and the post service calibrations, it would be possible to reconstruct any or all of the data collected to 'real' values.

SUMMARY

The ability to gather data, and to monitor processes, using electronic techniques provides opportunities for enhanced understanding of water quality. There are also the opportunities and risks associated with each company, agency, or scientist operating independently. Compatibility, particularly of data from different loggers and from different agencies, may mean that, in the future, many incompatible data will exist. Some efforts in standardization of sensors, software, and measurement (i.e., hardware) techniques could alleviate some of the potential problems. Is there a common solution or solutions? Inter-agency cooperation in maintaining proper documentation of all aspects would provide the necessary reference for the future. All agencies who gather this type of data would benefit from increased cooperation since many of the common problems and situations can be avoided (Spittlehouse, 1989). Common procedures need to be developed to assure the broader compatibility between agencies.

What is the optimum sampling frequency at which data loggers should operate? While off-the-shelf data loggers have some flexibility in allowing sample interval to be set, they usually treat all sensors equally. Such loggers may not provide the optimum operation of the loggers in relation to available memory. Programmable loggers can be used to design more effective sampling procedures; instruments, such as the CR10, can operate at more than one sampling rate simultaneously. Programmable logic may also be used to enhance such data collections, allowing enhanced sampling and storage during certain conditions. Sampling of this type could also be used to operate ancillary devices, such as sample collection devices or remedial equipment, during prescribed events. Crucial variables could have replicate sensors deployed, allowing for both a degree of redundancy and some insurance against sensor failure. Electronic data acquisition can provide opportunities for more efficient and effective water quality monitoring.

Electronic data acquisition offers many opportunities and challenges for the future of water quality monitoring. Our success in adapting and implementing data loggers to real world problems and situations hinges upon our ability to provide adequate quality assurance, and to maintain our instruments in a manner which provides good, well documented data.

ACKNOWLEDGMENTS

Several people have made significant contributions to our developments in data logging. Norm Dalley initiated the work in data logging, and Normand Rousseau did most of the implementation design. Eric Michnowsky provided expertise in quality control when it was much needed. Their influence and ideas have contributed significantly to the ideas and procedures presented here. The two sites described here are located adjacent to fish hatcheries in parks operated by the Greater Vancouver Regional District. The cooperation of the G.V.R.D., and the support of John Heaven at Kanaka Creek Hatchery and Frank Walden and his crew of volunteers at Tynehead Hatchery is appreciated. This manuscript was reviewed by Malcolm Clark whose comments and suggestions are appreciated.

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CYANIDE WORKSHOP UPDATE

Malcolm J. R. Clark

British Columbia

Ministry of Environment, Lands, and Parks

Nov 10/93

Follow-up Survey of speakers from Oct 9/92 Cyanide Workshop

-prepared for Malcolm Clark by Trevor Murdock, co-op student

Howard Singleton "Cyanide Water Quality Objectives"

Dec 9/92

-made recommendations on Thiocyanate toxicity studies (see pg 201-202 of 1992 Proceedings)

Oct 14/93

-received comment from Graham van Aggelan re Howard's recommendations (see attached)

Oct 19/93

-HS will send MC a copy of response to GV's inquiry
-GV away until Oct 26
-if more needs to be done on thiocyanate, Water Mngt cannot fund any further work at the moment

Benoit Godin "Cyanide Speciation and Toxicity"

Nov 8/93

-Asked NWRI in Burlington for opinion, got mixed feelings: "interesting, continue and we'll see"
-Has not pursued anything further since the presentation

Dorothy Jeffery "Waste Technology Centre Cyanide QC Study"

Oct 19/93

-Zenon has not had a chance to implement the methods presented as yet since no one has submitted relevant samples. However, if such samples are sent in, the new methods will be tried
-noticed that tables from her paper appeared under Malcolm's talk in the Workshop Report [confirmed by MC - apologies to DJ]

Malcolm Clark "Federal-Provincial CN RoundRobin Results" and "Bioassay Study of Photodissociation of Iron Hexa-Cyanide Solutions"

Oct 19/93

-nothing to add

-Some tables made up by Dorothy Jeffery of Zenon Labs which both DJ and MC talked about appeared under MC's report. These tables (pgs 53-56) should have been placed under DJ's talk with a note in MC's talk to see those pgs.

Bruce Carmichael "Aquatic Toxicity of Fire Retardant"

May 17/93

-MC received FAX from BruceC of message from BruceC to Wally McCulloch of Chemonics

May 19/93

-MC received draft copy of confidential BCR Report "Toxicity of Fire Retardants to Fish" from WM of Chemonics

May 20/93

-MC sent comments to BruceC re draft BCR Report to Chemonics

Oct 18/93

-toxicity report was done by BC Research funded by Chemonics at request of MOE: confirmed that toxicity increased when fire retardant exposed to UV light

-Chemonics was requested to rewrite the report, the rewrite is now available

-the standard MSDS Sheets for fire retardant are not accurate!

-guidelines for portable helicopter mixing sites updated by Chemonics and Monsanto to take into account what was learned from the Stone Creek spill

-a large file on the spill is available from Bruce Carmichael

Larry Pommen "The Similkameen Experience"

Oct 19/93

-reviewed Federal cyanide data

-levels have been below Water Quality Objective levels so the contamination problems seem to have been solved

Vic Jensen "Anomalous Cyanide Results from a Gold Mining Operation"

Oct 20/93

-not going to Qualicum

-more sampling has been done, Cyanide still present but at lower levels since the mine has been requested to modify procedures regarding placing of blasting materials with respect to waste waters
-has not written up anything though, and has no plans to, nothing else has changed
-Cyanide appears to be generated in areas of waste drop, probably from blasting medium, but uncertain

Jim Van Barneveld "Discrepancies in Cyanide Results for Replicate Vegetation Samples"
Oct 19/93
-done nothing, no intent to do anything further

Gordon Ford "The Non-Reliability of Cyanide Analysis"
Oct 19/93
-still not sure if problems of non-reliability are caused by Cyanide or not (this problem has been worked on since the 70's)
Oct 25/93
-GF has "Technical Guide for Environmental Management of Cyanide in Mining"
-available through Bitec Publications, Richmond

Rob Gilbert "A Comparison of Automated Cyanide Analyses"
Nov 10/93
-forwarded Draft of results to Steve Horvath
-might have a good way of separating Cyanide from Thiocyanate using Formaldehyde & $C0_2$ membrane to measure both separately
-haven't had time to implement yet, have setup to do it, but to do it properly would need grant money to fund
-plan to write a proposal asking for government money, will contact MC about this in future

Paul Whitfield "Workshop Summation"
Oct 19/93
-nothing to add

PROACTIVE QUALITY ASSURANCE FOR CONTRACTED ANALYSIS

Robin C. J. Sampson

Environment Canada

National Laboratory for Environmental Testing

Burlington Ontario

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

Canada Centre for Inland Waters, Burlington Ontario

- ? Why/when should you use contract laboratories?
- ? How should you go about selecting a contract laboratory?
- ? How can you determine what is a fair price for services?
- ? How can you determine if the services offered meet your need?
- ? How can you assess value for $$$ and net worth of product (data)?
- ? How do you know the data are adequate for your intended purpose?
- ? Can you rely on follow-up assistance (interpretation, testimony)?
- ? Isn't the best answer to have your OWN laboratory?
- ? How and what type of QA do you need - when is "enough enough"?
- ? How should QA best be reported to be most useful?
- ? How can lab QA best contribute to overall project QA assessment?
- ? Aren't "post mortems" FUN????

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

DATA QUALITY MANAGEMENT

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

DATA QUALITY MANAGEMENT

First some definitions

✓ QUALITY ASSURANCE

- Integration of intralaboratory and interlaboratory QC procedures, standardization and management practices into a formal coordinated effort with clearly assigned responsibilities and duties

✓ QUALITY CONTROL

- Application of prescribed practices to minimize the systematic and random errors involving personnel, instruments, reagents, supplies and methods of sampling, analysis, data handling and reporting

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

OPERATIONAL SCIENCE SUPPORT TO C&P PROGRAMS

- Private Sector Laboratories (Contract Labs)
- University Laboratories and Research Facilities
- Government (Federal) Laboratories

Advantages Disadvantages

BUT

They offer different elements of needed science and have different "bottom lines"

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

OPERATIONAL SCIENCE SUPPORT TO C&P PROGRAMS

- Government Laboratories Have A Mandate to Deliver Against Political Priorities
- University Laboratories and Research Institutes are Focused on the Pursuit of Knowledge (AND $$$)
- Private Sector (Contract) Laboratories Are Driven by the "Bottom Line"

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LABORATORY QUALITY ASSURANCE

Every program group should have its own lab to carry out their analysis and thereby eliminate quality control as a variable or concern.....

Or should it??????

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

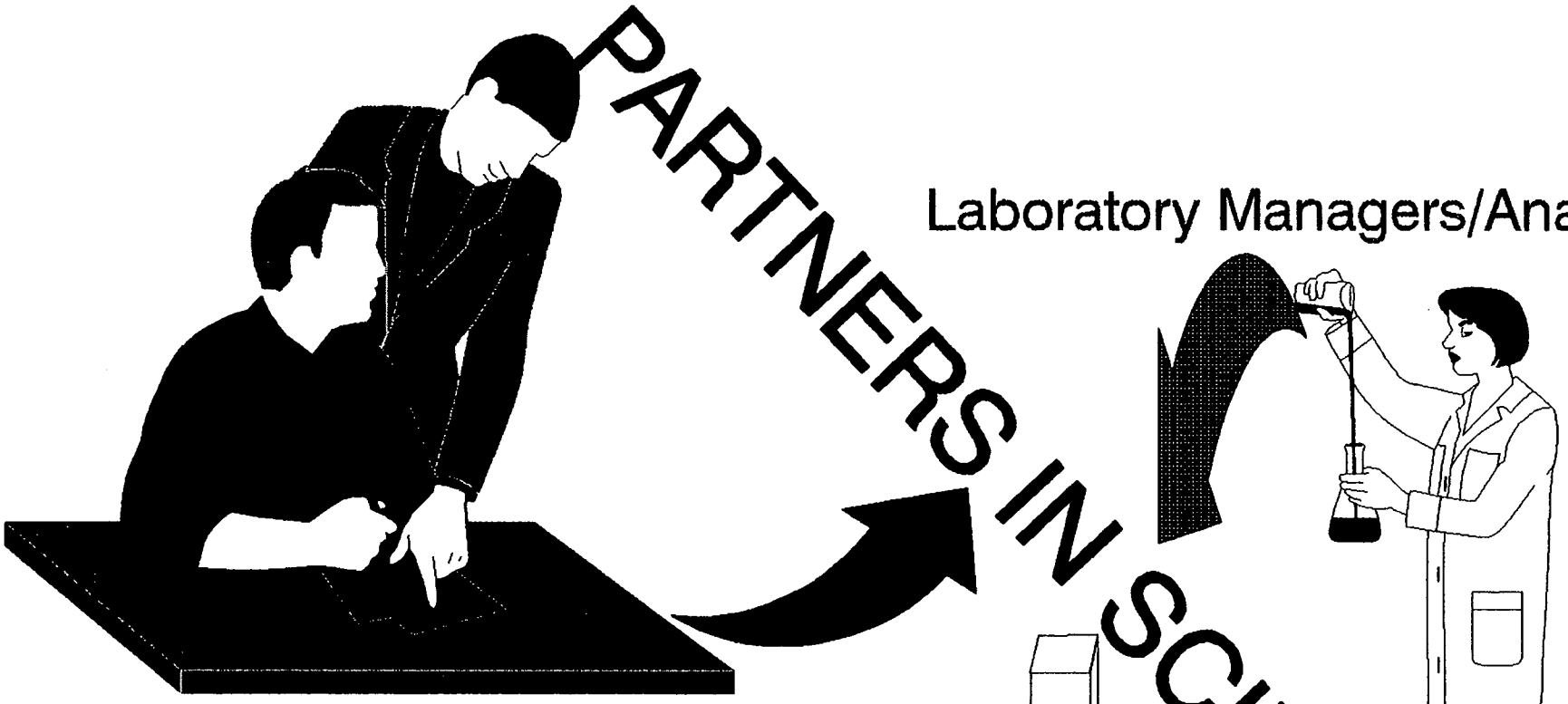
OPERATIONAL SCIENCE SUPPORT TO C&P PROGRAMS

- C&P LABORATORY MANAGERS COMMITTEE (LMC)
- CANADIAN ASSOCIATION FOR ENVIRONMENTAL ANALYTICAL LABORATORIES (CAEAL)
- NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING (NLET)

Tools You Can Use

1 These groups can help program/project managers Plan for and achieve success?

Successful program delivery in science means.....



Laboratory Managers/Analysts

Project Managers/Officers

(defined) **QUALITY = SUCCESS**

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

ROLE/PROGRAM DELIVERY MECHANISM - C&P LABS

- ✓Program Planning (DQO, Cost Effective Solutions)
- ✓Methods Development - Performance Guidelines - Integration of Information
- ✓In House Expertise/Capability
- ✓Contract Management
- ✓Field Support/Interpretation
- ✓Certified Expert Testimony
- ✓Service Wide Networking
- ✓Technology Development Transfer
- ✓Promotion of CAEAL
- ✓INDUSTRY DOES IT

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

ORGANIZATIONAL RESPONSE

- Program Development and Operational Support
- Research Support and Methods Development
- Analytical Chemistry

Other components to success than simply samples in, test results out (NO FUTURE!)

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

DATA QUALITY OBJECTIVES AS THE BASIS FOR EFFICIENT JOINT PLANNING

- Specific Limits on Uncertainty
- Clearly Stated Study Objectives
- Efficient Resource Expenditures
- Framework for Organizing Complex Issues

OWNERSHIP

PARTNERSHIP

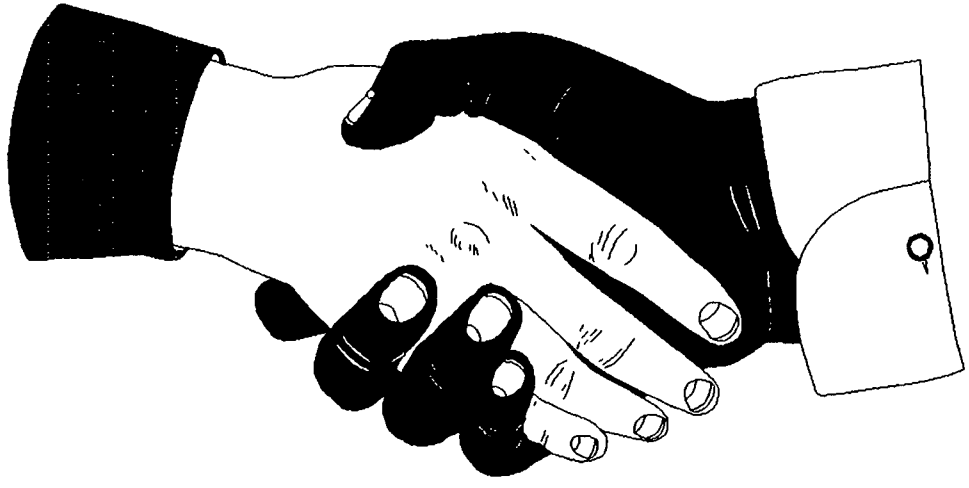
COMMUNICATION

2 This guidance manual can be shared by project and laboratory managers for definitive exploitation of contract analysis opportunities

CONTRACTING MADE EASY

LET'S MAKE A DEAL

HAPPINESS IS QUALITY



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PREQUALIFICATION OF CONTRACT LABORATORIES

- CAEAL Accreditation/Certification What do they mean?

- Congruence with "Partner" Laboratory (Splits, Brokerage, Subcontracting)

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NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

THE CONTRACTED LABORATORY SERVICES MANUAL

Standardized "Table of Contents"

- Prequalification of Contract Laboratories
- Requests for Proposals
  - Information Provided TO Contractor
  - Information Provided BY Contractor
- Contract Assessment and Supplier Selection
- Contents of Contract Document
- Contract Management and Monitoring

(CAEAL course)

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NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

Information Provided TO Contractor

- Description of Project
- Description of Services Required
- Details of Proposal Submission

Information Developed from the DQO Exercise

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Information Provided BY Contractor

- Analytical Protocols and Procedures
- Quality Assurance/Control
- Contract Laboratory Qualifications
- Pricing and Scheduling
- Data Reporting

DID CONTRACTOR UNDERSTAND?

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

Contents of Contract Document

- Project Objectives, Purpose, Background
- Purpose/Focus of Analytical Results

- Detailed Logistics
  - Analysis Specifics
  - Methods and Quality Assurance
  - Load Split and Interactive Details
  - Reporting Details (including deadlines)

This is your Mini Business Plan

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

Contents of Contract Document

- Project Objectives, Purpose, Background
- Purpose/Focus of Analytical Results

- Detailed Logistics
  - Performance
  - Dispute Resolution
  - Interlab Participation

This is your Mini Business Plan

ENVIRONMENT CANADA

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CONTRACT MANAGEMENT AND MONITORING

- Data Quality Assessment
- Interactive Correction
- Site Inspections
- Audits
- Schedules and Budgets

With the help of your friendly neighbourhood gov't lab partner

3 This is how the NLET is automating data quality management for contracted testing services

SWITCH
(A production of the NLET bringing partners and parents together)

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(ECO)LABORATORY INFORMATION MANAGEMENT SYSTEM

- Project Management and Accounting
- Sample Management
- Data Acquisition/Data Management

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NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

ECOLIMS ACQUISITION PROTOCOL - QC

- Data From Instruments in "TRAYS"
- QC Aliquots Predefined: LOCATION TYPE VALUE
- Preliminary QC Report - Operator - Update/Corrective Action
- Approval - Update SAMPLE Database/QC Database

ENVIRONMENT CANADA

NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

SETUP - CONTRACT PERFORMANCE MONITORING

- Define Method/QC Characteristics with Contract Laboratory
- Assign Unique Method Codes for Contract Laboratory
- Define and Establish Communications (Data Transfer) Protocols

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DATA DELIVERY STAGES OF ECOLIMS

- LOGIN
- Worksheet Generation
- Analysis
- Data Transfer (Entry)
- Data Review
- Reporting

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ECOLIMS - QC DATABASE

- Date/Time
- Operator
- Method
- Tray
- Associated Sample Identifiers
- Value
- Flags

"LIVING" QC DATA BASE CONTAINS CONTROL INFORMATION FOR EACH QC TYPE, EACH PARAMETER

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NATIONAL LABORATORY FOR ENVIRONMENTAL TESTING

UNIQUE ECOLIMS QC DATABASE FEATURES

- Unique Method Codes Identify Each Method for Each Parameter for Each Laboratory
- Unique Project Number Identifies Each Client (Activity)
- Each Test on a Sample is Linked to All QC Data Associated with that Test
- CONTROL LIMITS TABLE Stores Limits and Other Control Information for Each QC Type for Each Parameter
- QC DATABASE Stores and Reports ALL QC Information for Each QC Type for Each Parameter
- "Preliminary" QC Report Governs Analyst Interaction Prior to Sample Database Updating
- "Comprehensive" QC Reports Provide Analysts AND CLIENTS with QC Data Historical Reviews by Method or Sample

- √Environmental Science Officers Manage Programs Whose Success Is Predicated on Meaningful Laboratory Measurements

- √Laboratories Are Expensive, Complex Beasts with Organizationally Dependent "Bottom Lines"

- √How Can One Achieve Meaningful, Cost Effective Delivery?

FIELD QUALITY ASSURANCE FOR ORGANIC CONTAMINANTS

A Discussion

Taina Tuominen

Environment Canada

Pacific and Yukon Region

Field Quality Assurance for Organic Contaminants

A Discussion

T. Tuominen informally discussed sampling methodology used in studies conducted by the Environmental Studies Division of Environment Canada. The discussion focused on current sampling for contaminants in suspended sediments and work in river systems. Equipment preparation, duplication, and QA procedures by the lab were also discussed.

DATA VALIDATION AND APPROVAL PROCEDURES

Paul H. Whitfield

Environment Canada

Pacific and Yukon Region

Data Approval and Validation

Paul Whitfield

The Data Approval Work Group is developing a process which provides a basis for agencies to move from a view - "Any Data is Good Data" to one where "Data is of a known and recorded Quality". In developing the process we initially established a set of principles which form the basis from which the process would be developed:

- all data should be in the public domain
- data validation should not delay availability
- data is a valuable corporate resource
- need to know who is using the data
- feedback mechanism from users
- credit to the funding agency
- issue of ownership needs to be addressed
- user is responsible for application
- issue of copyright needs to be addressed
- data is a shared responsibility
- value of data is increased through approval process
- data needs to be good for decades
- data is of value to multiple persons/agencies
- records must be kept for long periods of time.

Validation

The validation processes being developed recognizes that the validation processes needs to use QA data and release it; therefore QA data must be public. The results must be documented with a real paper original; paper trail for corrections - include both field and lab. All errors must be recorded and corrected as part of paper trail. Questionable data is to be flagged. There will be a 'paper' record of the validation which records the approval, and records what was found and what was done.

It has been agreed that it is important to flag data to mark different types; and such flagging would be applied to values,

observations, and records. Flagging would indicate suspect, validated, repeated measures, non-conforming. The application of flagging needs to:

- empower people
- be consistent
- be concrete
- convey information

Approval

Approval is the confirmation that the data collected meet certain standards. It requires the signature of the person designated to approve the data. The work group envisages this as two parts:

- ongoing review and screening of incoming data
- formal approval no less than once per year

The approval will be based on observations, laboratory qa reports, and field qa program results. The validation and approval process needs mechanism for ongoing changes through peer review

Process

APPROVAL

- collect and record substantiating data
- work within a set of rules
- classify data on adherence to rules

poor, fair, good, excellent

AUDIT

- audit on a random basis
- selected stations
- check for consistency with process

STANDARDS

Ian McLaurin

Environment Canada

Headquarters, Ottawa

STANDARDS FRAMEWORK TEAM

Ian McLaurin	Water monitoring standards
Nik Lopoukhine	Parks data collection
Connie Downes	Non-game bird surveys
Shelia Forsyth	Environmental Effects Monitoring
Shirland Daniels	Laboratories
Dave Dockendorff	Weather and air monitoring

Regional and SOE reviewers

Environment Canada Environnement Canada

Ian McLaurin

Head, Standards, Coordination and Training Section
Monitoring and Surveys Division
SISB/ESED/C&F

Office Address: 8th Floor, PVM
351 St Joseph Blvd., Hull, Quebec

Mailing Address: Ottawa, Ontario K1A 0H3
TEL: 819 997-2099 FAX 819 994-1691

Canada

TERMS OF REFERENCE

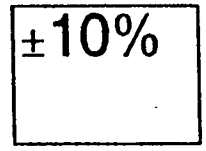
Develop a **framework** for the development of standards in the acquisition, analysis and processing of data and information.

Develop a **process** to ensure the regular review of departmental standards.

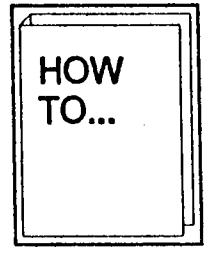
DEFINITION

Standards are agreements that the specified activity is to be done by;

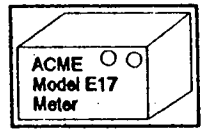
- measuring to a certain accuracy and precision,



- following a defined procedure or methodology,

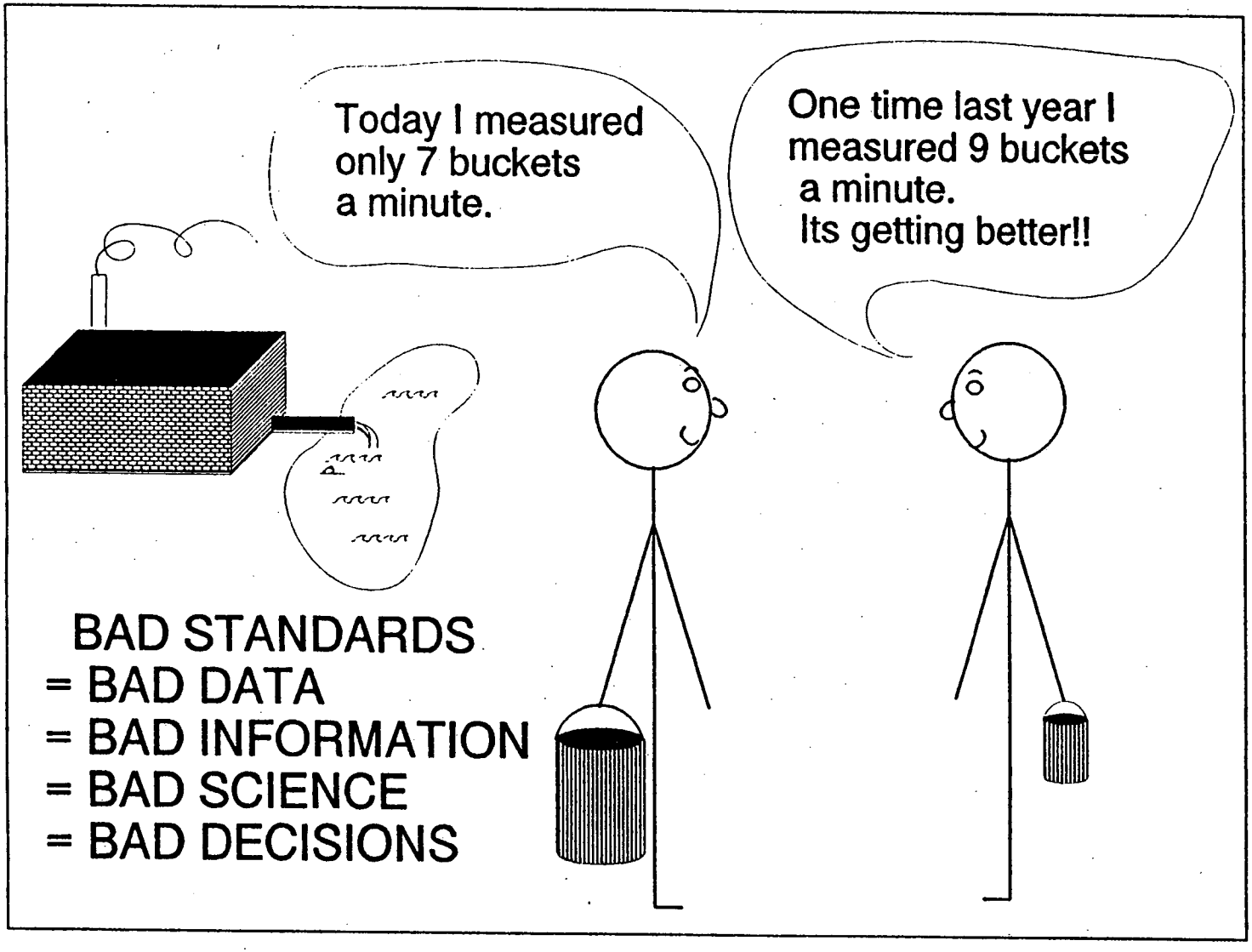


- or by using selected equipment or reference materials.



Standards can apply to all monitoring activities from planning to information dissemination.

IMPORTANCE


Today I measured only 7 buckets a minute.
One time last year I measured 9 buckets a minute. Its getting better!!
BAD STANDARDS
= BAD DATA
= BAD INFORMATION
= BAD SCIENCE
= BAD DECISIONS

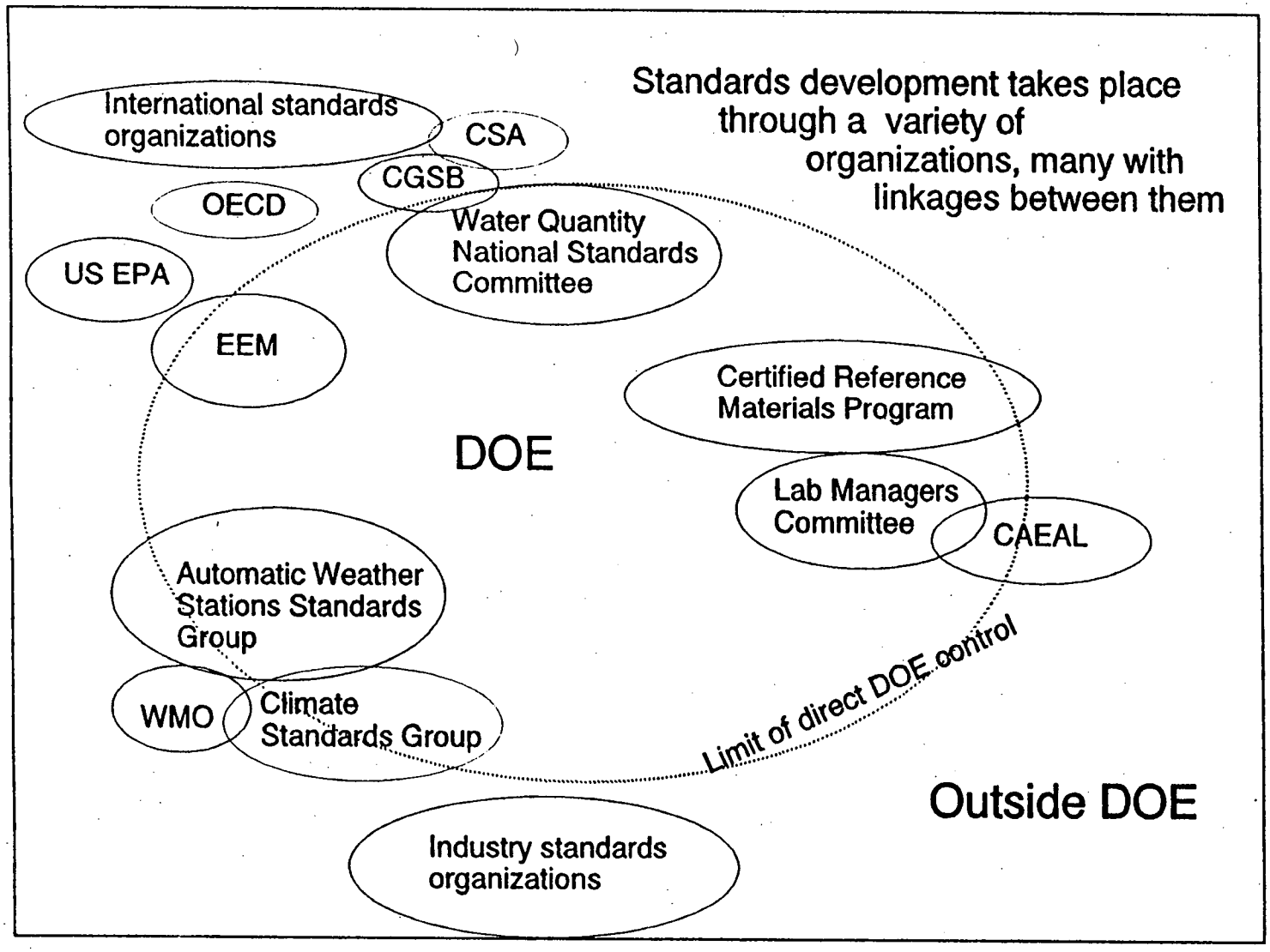
STANDARDS DEVELOPMENT

Basic framework

- form long term committee of interested parties
  - regularly examine need for new or revised standards
    - assign task of developing draft standard:
    - review of draft by committee
  - agreement on acceptance or rejection of draft
  - produce and disseminate the approved standard.

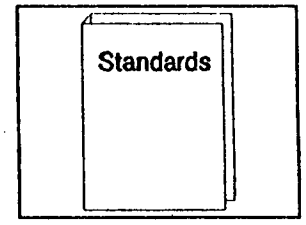
Used by existing committees and groups wholly or partially in DOE monitoring.

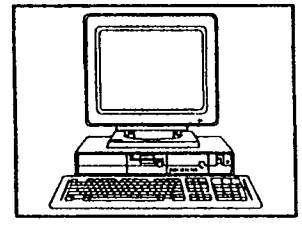
EXISTING SITUATION



TO FACILITATE INTEGRATION (1)

Information exchange
- descriptions of monitoring programs,
  opportunities for sharing
- inventory of experts,
  access to other sectors
- list of standards.
  comparable data/information





Information will be used by managers of monitoring operations to meet resource and client requirements

TO FACILITATE INTEGRATION (2)

Guidance
- to widen standard setting groups
  meet more needs
- to incorporate integrated strategies
  ecosystem approach
- to relate monitoring standards to needs
  appropriate effort

Planning, operations, and assessment are integrated
Measurement remains sectorial

PROCESS COORDINATED BY COMMITTEE

Environment Canada Standards Committee

Members from operational DOE monitoring standards groups coordinating their activities;

1 to develop and provide tools for integrated standards development and use

2 to serve as point of first contact for standards concerns

3 to review plans for major monitoring initiatives to ensure that any standards gaps are addressed

PROPOSED ACTION PLAN (93/94)

- form the Standards Committee
 - refine the standards framework (June 1993)
 - draft procedures for information exchange (June 1993)
 - hold a departmental standards workshop (Oct/Nov 1993)
  to discuss standards framework
  to develop common vocabulary
  to identify opportunities
 - initiate mechanisms to facilitate integrated standards development and use. (Dec 1993)

CONSERVATION AND PROTECTION | CONSERVATION ET PROTECTION

MEMORANDUM | NOTE DE SERVICE

TO / À: Distribution list / Liste de diffusion	Security-Class.-Sécurité
	Our file/Notre référence
FROM / DE: Chairman, Standards Framework Team / Président de l'équipe chargée de l'élaboration d'un cadre pour les normes	Your file/Votre référence
	Date September 16, 1993

SUBJECT / OBJET: Integrated Monitoring - Standards Workshop - November 24-25/ Atelier sur les normes - surveillance intégrée - 24 et 25 novembre

The purpose of this memo is to announce a Department of the Environment Standards Workshop for November 24, 25 in Toronto.

Cette note de service vise à vous informer de la tenue d'un atelier sur les normes du ministère de l'Environnement qui se tiendra à Toronto du 24 au 25 novembre.

As part of the Integrated Monitoring initiative a Standards Framework Team was formed and tasked to develop a framework for the development of standards and to develop a process for their maintenance. The outline of that standards framework will be included in the Integrated Monitoring Business Plans scheduled to be completed by this September. These plans will put forward the overall departmental strategies for environmental monitoring while meeting the demands for integration, ecosystem approaches, modernization, products and services. Standards will play a key role.

On a formé, en tant qu'initiative reliée à la surveillance intégrée, une équipe chargée de l'élaboration d'un cadre pour les normes. Elle devra élaborer un cadre destiné à l'établissement des normes et d'une procédure nécessaire pour les mettre en vigueur. L'ébauche du cadre fera partie des plans d'entreprise en matière de surveillance intégrée prévus pour le mois de septembre. Ces plans mettront en évidence toutes les stratégies ministérielles reliées à la surveillance intégrée satisfaisant aux demandes concernant l'intégration, les approches écosystémiques, la modernisation, les produits et les services. Les normes joueront un rôle important.

The Standards Framework Team is inviting you to the workshop (see attached). The purpose is to develop a path forward, in practical terms, to implement the recommendations of the Business Plans as they apply to standards.

Les membres de l'équipe vous invite à y participer (voir la pièce jointe). Cet atelier vise à élaborer une approche, à savoir la mise en oeuvre des recommandations des plans d'entreprise reliés aux normes.

As you know, standards can specify that monitoring is to be done to a certain accuracy and precision, or to a certain methodology, or by using specified equipment or reference materials. This makes the collected data and information more usable,

Comme vous le savez, les normes peuvent spécifier l'exécution de la surveillance à une certaine précision ou selon une certaine méthodologie ou finalement par l'utilisation de matériel ou documents de référence spécifiques. De cette façon, les

accessible and comparable with benefits to both the science and management of monitoring programs. Standards have, for the most part, been developed by headquarters offices for national programs. The regional integration of our monitoring operations and the shift towards ecosystem approaches is already having an effect on the process.

données recueillies seront plus valables, accessibles et comparables et, de ce fait, le domaine des sciences et de la gestion des programmes de surveillance plus avantagés. L'établissement de la grande majorité des normes revient aux employés des bureaux de l'administration centrale responsables des programmes nationaux. L'intégration régionale de nos activités de surveillance et l'accent mis sur les approches écosystémiques ont déjà eu des conséquences sur la procédure.

Please circulate this invitation to your colleagues. You may also invite your counterparts in provincial and other agencies. If you have any suggestions for speakers or discussion topics please feel free to provide them.

Veuillez faire circuler cette invitation à vos collègues. Vous pouvez également inviter vos homologues des provinces et d'autres organismes. Si vous avez des suggestions relativement aux conférenciers ou aux thèmes de la discussion, veuillez me les communiquer.

Ian McLaurin

WORK GROUP

PRESENTATIONS

(Overhead slides transcribed by Norman L. Wade)

Work Group I - Don Morse

REFERENCE SAMPLES

- 'BLIND' - WHY
    - Essential QA Element
        - More Of A 'NORMAL' Sample.
- Sources + Types Are Limited
    - NWRI
    - NRC - Marine Sediments
    - EPA - Certified Standards
- Requires Facilities To Make Program Samples
    'Appear" Blind
- Standard Reference Material (SRM)
- Limited Availability - Expensive
- Can Provide Long Term Assurance

Work Group II - Ian McLaurin

Field Safety

- Chemicals, Remote areas, Water,

  Equipment, Flying, Driving, Etc

- Training Materials / Manuals

  C & P / Dept. Manual

- Traiming Before field work

- Proactive Management Activity

  - Training

  - Checking

  - Retraining

- Use Health and Safety Committees

- Report close calls

- Lay People

Work Group III - Larry Pommen

FIELD FILTRATION / CLEAN METHODS

& EVERYTHING ELSE

FIELD FILTER: (or) NOT!

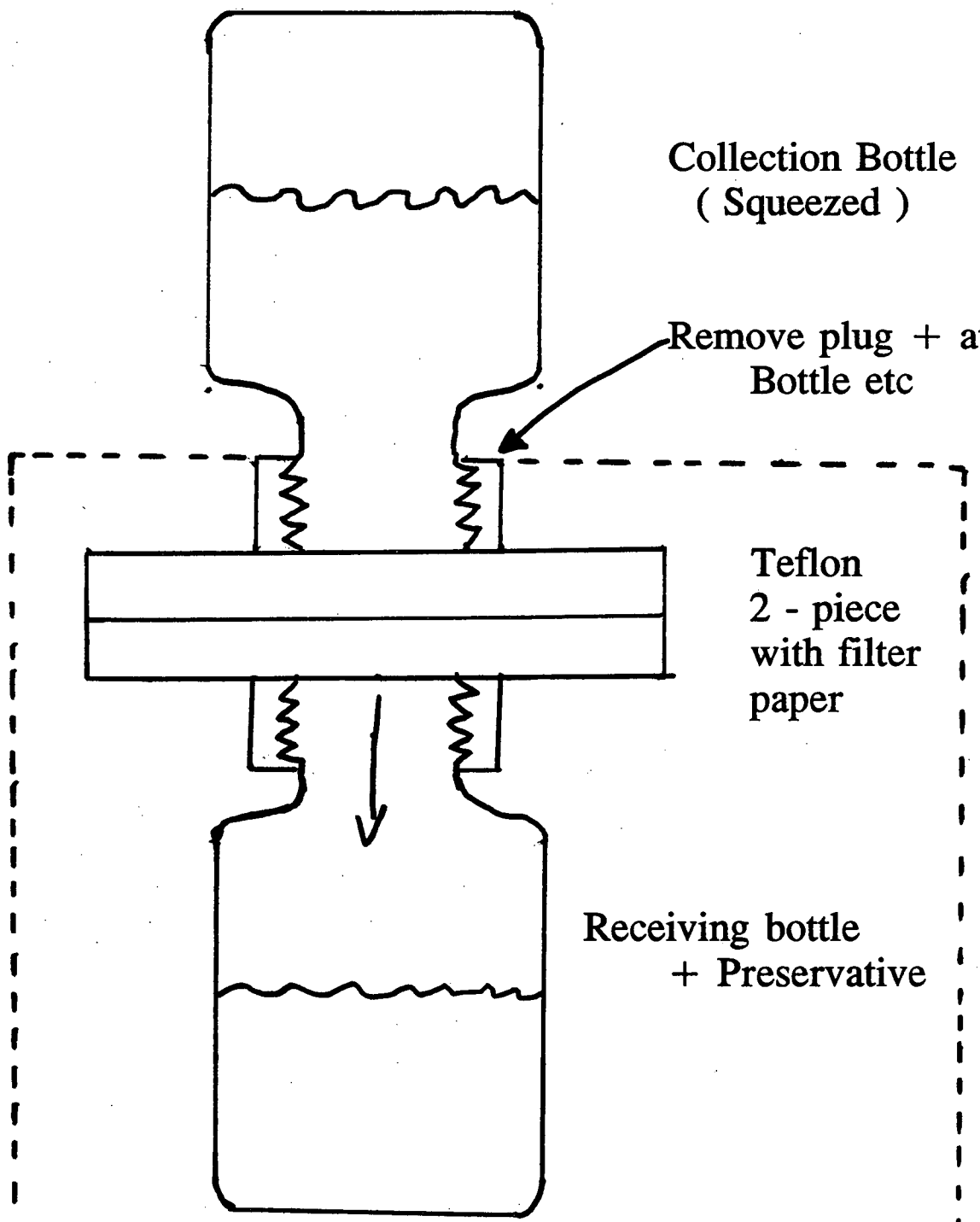
- Depends on every factor you can think of, but.....
- Need resourses to develop / implement
- Use NWRI expertise
- Sea Star prototype - Lay Collectors

CLEAN METHODS: YES! or Quit.

- Comparison of McRae vs. Ryan
- Just do it, e. g., double bags

clean thru - ice bottles

SEASTAR MODEL



Prepared & Shipped from Lab; Returned
by Collector (double bagged)

Work Group IV - Dorothy Jeffery

Contract Labs

1. Continuity (of) data

2. Validation of data between labs

   - methods

   - performanced based

   - Interlab QC
     - Blind Samples
     - Lab Accredited

3. Report format

   - driven by government std

   - QC data
     - batch

4. Fed. government contracts approved by Fed. Lab staff

   - Need feedback

5. Sub-contracting, side contracts

6. Data associated to lab id.

7. Uncertainty in

$$X = T + E_1 + E_2 + E_3 \ldots\ldots\ldots$$

in Batch QC

8. Documentation std. for methodology

9. Encourage giving contract to archive method documentation

D. Jeffery notes* from Oct. 28, 1993 meeting with Dorothy Jeffery, Henry Quon, H. Nguyen, Norm Wade and Malcolm Clark.

Contract Labs

1. Continuity of data
   - overlap period of labs for real samples

2. Validation of data between labs

3. Standard procedures, eg., BCMOE new manual
   - method development
   - performance based methods (how evaluated?)
   - DL, precision, and accuracy to be reported for each sample

4. Private clients usually are reporting to government agencies so government standards will apply to private/contract labs

5. Federal government (especially in organics) gives out contracts with approval by federal lab staff to a certain standard

6. Contract labs participate in inter-lab QC studies
   - funding of studies by contracting agencies not contract labs

7. Blind samples - some are made without proper equipment, proper chemicals (stability contamination free), proper techniques, proper interpretation - some/all blind samples have no credibility

8. Lab Sub Contracting
   - labs now are specializing or limit their scope therefore subcontracting may be a plus.

9. MOE side contracts outside main lab contract and have no QC!

10. Certifying agencies is to a minimal lab performance level but may not cover parameters needed, or you may want a higher performance.

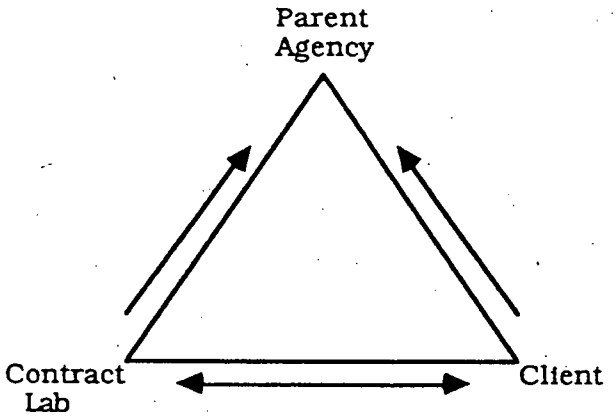
11. No contracts let by Environment Canada; future ones will be checked by C&P lab (Henry Quon, Randy Engler, Paul Kluckner).

12. Contract labs of any type must have access to historical data for validation checks.

13. Feed back from contract lab should be via original approving person

14. During term of contract, communication should go to client from contract lab.

* edited by MC



Interaction Diagram

15. Batch QC to be recorded with data on reports or at least be available in separate/relatable computer file:

- calibration line/points - linearity
- calibration control
- blanks & method (if appropriate)
- replicates
- ref. material, or spike, if appropriate
- surrogate recovery (organics).

16. Sources of data uncertainty:

- linearity
- precision
- sample stability
- preparation recovery
- etc.

17. Technology transfer

MERCURY ISSUES

Larry W. Pommen

British Columbia

Ministry of Environment, Lands, and Parks

Summary

The accurate measurement of mercury in water is very difficult because it is present in extremely low concentrations in the water phase (e.g., 1 ng/L total mercury in unpolluted water; 5-10 ng/L in polluted water; Bloom, 1989, Watras et al, 1990) (1 ng/L = 1 part per trillion =10^{-12}) and is subject to artificial contamination from many sources, including mercury vapour in the air. Improvements have been made in the way we measure mercury in water in BC, but further improvements are needed before meaningful low-level results can be obtained. Present methods are prone to contamination and are not sensitive enough to measure significant levels in water.

History

The Quality Assurance Work Group of the Canada - BC Water Quality Agreement began addressing the issue of mercury measurement in water in October, 1987. At this time, the BC Environmental Laboratory was using common polyethylene (PE) sample bottles and bulk dispensers for preservatives, while Inland Waters of Environment Canada was using teflon sample bottles and single-sample glass vials with teflon-lined Bakelite lids to dispense preservatives. Environment Canada (1981, Brooksbank, 1985) and Fisheries and Oceans (Thomas, 1986) publications recommended the use of glass sample containers because mercury vapour passes through PE, and some doubts were expressed about teflon containers. A literature search by the federal and provincial labs in 1988 indicated that glass was best, teflon was satisfactory, and common PE was unsatisfactory. The BC lab - about to be privatized- refused to change from PE because of concerns about glass breakage and the cost of teflon bottles. The BC lab was taken over by Zenon Environmental Laboratories in 1989, and the mercury issue was submerged by numerous transition problems until late 1990.

Literature searches by Zenon and the BC Water Quality Branch led to the use of glass bottles and single-sample glass preservative vials with teflon-lined lids in late 1991. Meanwhile, Inland Waters began to experience contamination from their glass preservative vials with teflon-lined Bakelite caps in the late 1980's. The vials were being reused and over time the teflon liners deteriorated, allowing the preservatives to contact the Bakelite lid, imparting mercury, cyanide, copper, lead and zinc to the preservatives and samples. These vials were replaced by polypropylene vials in early 1991, but polypropylene is also pervious to mercury vapour, and Inland Waters is currently searching for a suitable glass/teflon replacement. Also, in 1993 we discovered that the Environment Canada Conservation and Protection Laboratory in West Vancouver is still using PE sample bottles.

The BC Water Quality Branch has used Analytical Services Laboratories (ASL) for its ambient surface water mercury analyses since 1991. ASL uses glass bottles with teflon-lined lids and has a comprehensive field/lab QA program, but the preservatives are dispensed in bulk from a PE bottle using PE pipettes. CanTest Laboratories will take over from Zenon for routine mercury analyses for BC Environment in 1994, but the lab to be used for the Water Quality Branch's analyses has yet to be selected.

Sample and Preservative Containers

The lessons learned about sample and preservative containers are:

- Mercury contamination significant to levels in water is everywhere - in the air, dust, dirt, lab water and acids (Figures 1 to 5).
- Mercury vapour in the air is literally sucked from the air into acid preservatives and acidified samples (Figure 6).
- Glass (borosilicate or quartz) and or teflon **must** be used; they are impervious to mercury vapour; polyethylene, polypropylene, and vinyl are not (Figures 7 and 8).
- Containers **must** have tightly sealing caps since mercury vapour will go up the threads and into the sample or preservative (ultra-clean method uses a wrench to tighten lids!).
- Bulk preservatives should not be used; opening the preservative container many times invites contamination, as does repeated insertion of pipettes. The risk of contamination increases with the length of exposure to potentially contaminated atmospheres.
- Use fresh, single-sample aliquots of preservatives.
- Teflon containers are preferred over glass for ultra-clean work; can be cleaned better, lids seal better, light, unbreakable, and the life-cycle costs are similar (Figure 9).

Normal Sampling Methods

- Collect surface samples **directly** into clean sample bottles.
- Collection of samples from depth is a problem; discrete samplers such as Van Dorn, Niskin, GoFlo, and Kemerer grossly contaminate samples at the ng/L level even under the best conditions (Figure 10). See ultra-clean sampling methods.
- Minimize exposure of open bottles and preservatives to the air.

Ultra-clean Sampling Methods

To decrease mercury detection limits to the sub-ng/L levels so that the actual levels in water can be measured will require not only an improvement in laboratory methods, but also the adoption of ultra-clean sampling methods. According to Brooks Rand (1990) and the Wisconsin Department of Natural Resources (Knauer, 1991), these include:

- Stringent bottle washing and handling; double bagged in clean PE bags.

- Two-person sampling crew; one "clean hands", one "dirty hands".
- Clean room gloves (new ones for each sample or unclean contact), suits and hats for sample collectors.
- Cleaned, plastic sampling boats.
- Pump sampling for samples from depth (e.g., cleaned teflon tubing/peristaltic pump or cleaned vinyl with high-volume pump).

Mercury Levels, Detection Limits, and Criteria

Mercury levels in unpolluted waters have steadily fallen as more sensitive and cleaner measurement methods have been adopted as shown in Figure 11. Unpolluted waters typically contain about 1 ng/L total mercury, while polluted waters contain 5-10 ng/L (Bloom, 1989, Watras et al, 1990). Figure 11 also shows that the detection levels used in BC have been, and continue to be inadequate to measure these levels. Five ng/L is the lowest detection limit currently used, which is not adequate to measure polluted or unpolluted levels accurately. A detection limit of about 0.1 ng/L is needed so that levels in the 1 ng/L range can be quantified with reasonable certainty. Figure 12 shows the detection limits that are attainable with ultra-clean methods versus typical levels in uncontaminated waters for various mercury species. Mercury speciation will become increasingly important as our understanding of mercury cycling and toxicity increase.

Our data bases contain numerous mercury values above the various detection limits used (5-50 ng/L); my contention is that most of them represent nothing more than artificial contamination and uncertainty close to the detection limits. We should either improve our detection limits by adopting ultra-clean methods or abandon trying to measure mercury in water - efforts would be better directed at effluents, biological tissues, and sediments where higher concentrations reduce the influence of artificial contamination.

The water quality criteria for total mercury in water are a maximum of 100 ng/L and an average of 20 ng/L (Nagpal, 1989; CCREM, 1987)(Figure 11). Given the past difficulties of accurately measuring mercury and the knowledge that polluted levels are much lower than the criteria, I expect that criteria levels will fall in the coming years. Wisconsin is adopting criteria that limit the **increase** in the mixing zone of waste discharges to 2 ng/L (Knauer, 1991).

Quality Assurance Samples

Analytical Service Laboratory Ltd.(ASL), which has analysed the Water Quality Branch's ambient mercury samples since 1991, has an excellent program of QA samples to define precision and accuracy and to demonstrate contamination control. For each batch of ≤10 real samples the following QA samples are analysed:

- A method blank (a lab blank of all the steps in the method)
- A duplicate (repeat measurement on a real sample)

- A travel blank (a preserved blank that travels to the field and back unopened) or a field blank (an unpreserved blank that is opened and preserved in the field)
- An "archived" travel blank or field blank (blanks that remains in the lab-same batch as the ones that go to the field)
- A field spike
- An "archived" field spike (prepared at same time as field spike and retained in lab to check for analyte degradation)
- A certified reference material

All of these QA results are reported with the results for the real samples in the batch.

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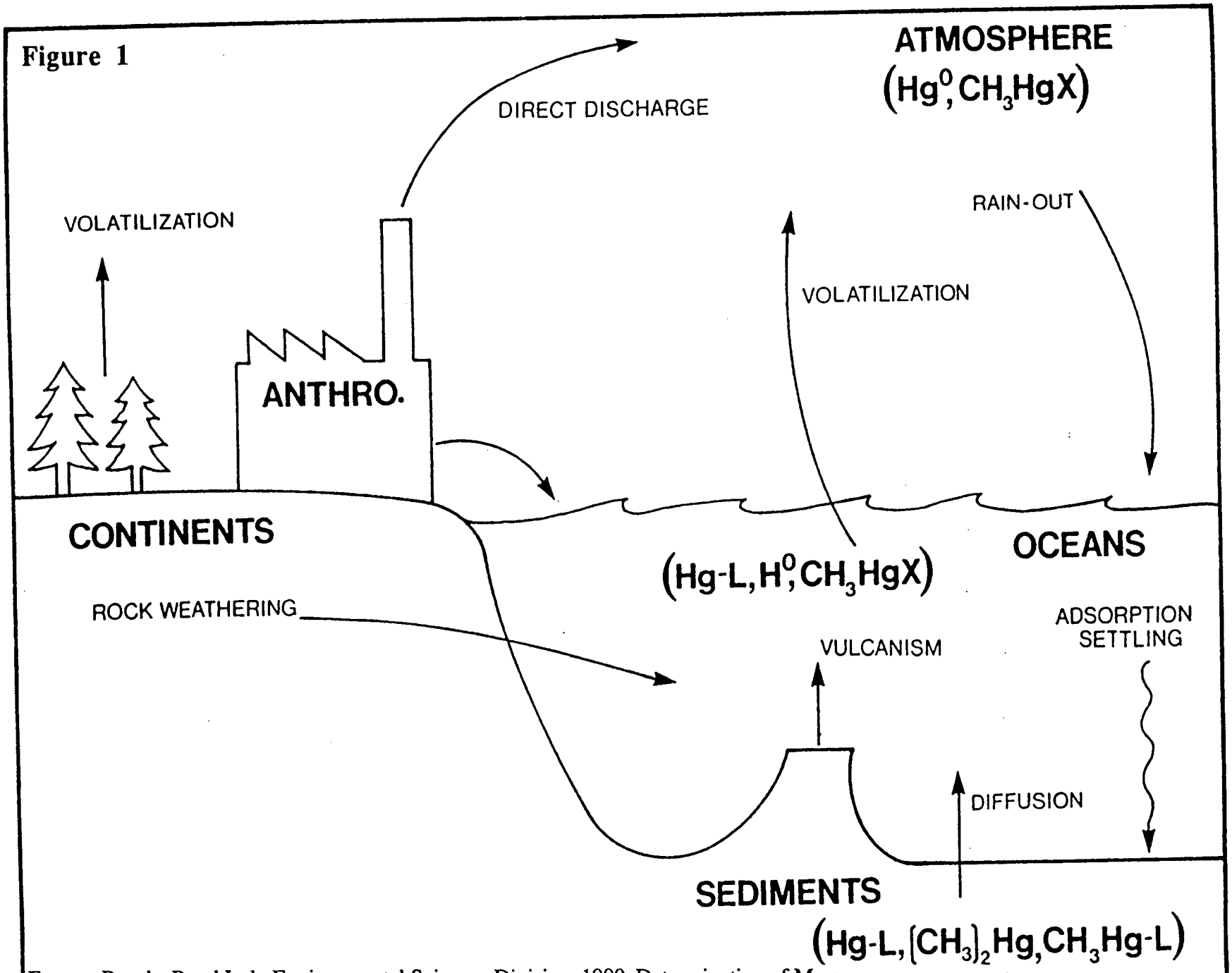
Figure 1



From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

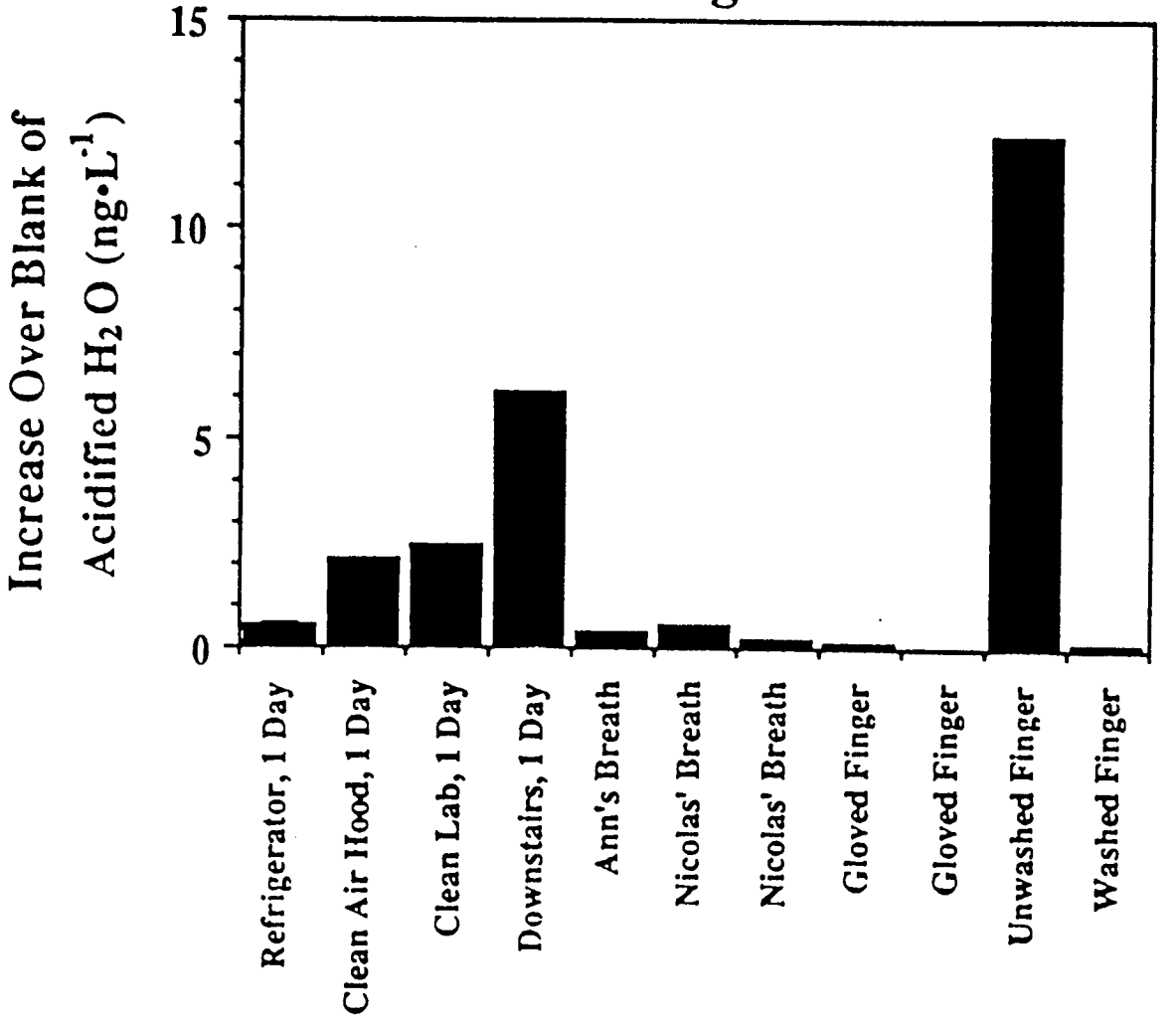
Figure 2

CLEAN-UP OF LAB AIR FOR LOW LEVEL Hg ANALYSIS

Initial Condition:	$[Hg_t]$ $ng \cdot m^{-3}$
Closed room, old paint, used lab benches	320
Ventilate with outside air	79
Cover old paint containing Hg	60
Remove contaminated sinks	15
Final Condition:	
Gold filters on clean air benches, venting outside air	
• Room air (varies)	2-10
• Clean Hood air	1-2
Outside Air, Seattle:	3-15

From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 3 **Magnitude of Various Potentially Contaminating Activities**



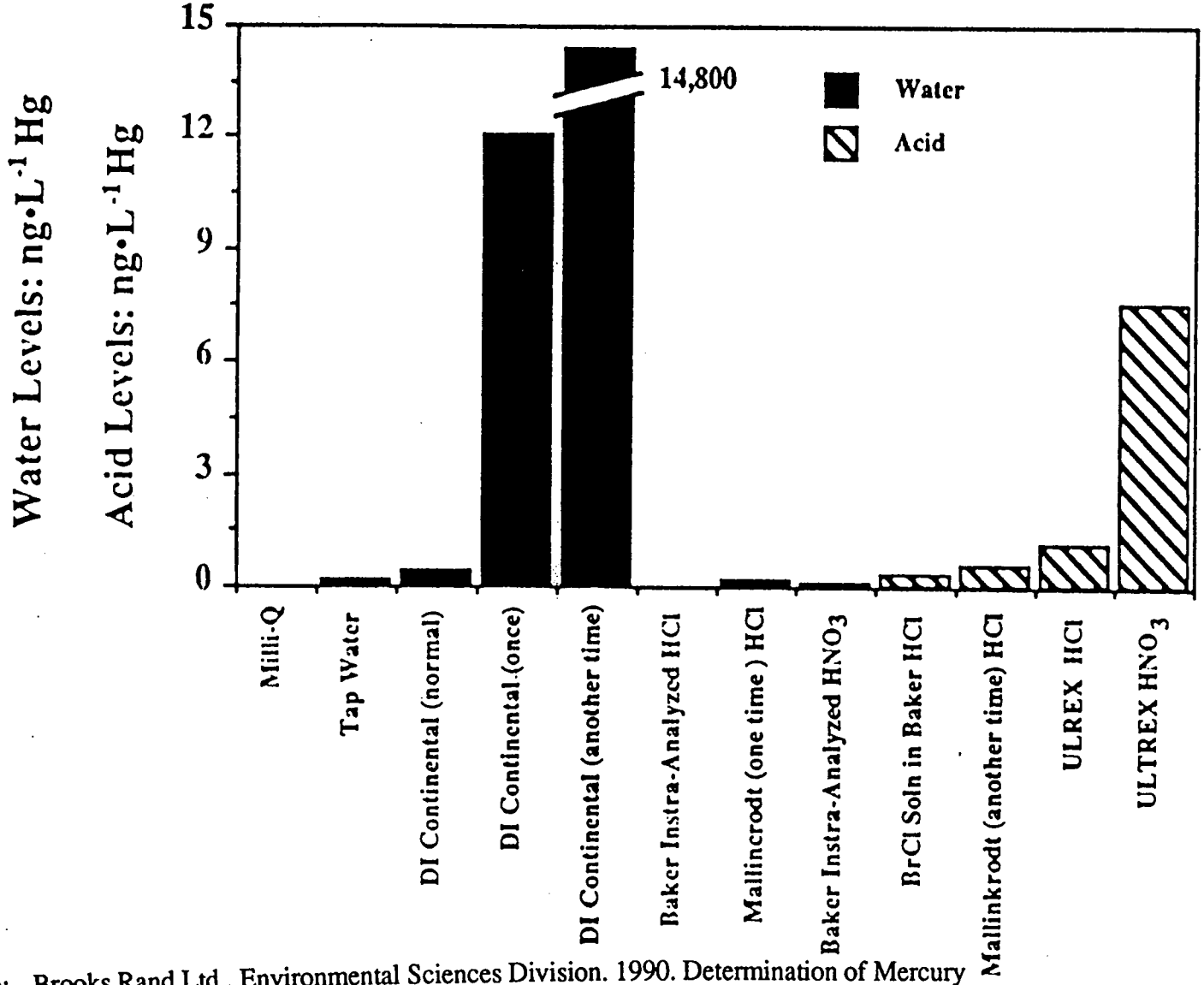
From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 4 MERCURY IN ROOM DUST

Dust Type	Hg levels, $ug \cdot g^{-1}$ Hg Total	Methyl	Percent Methyl
Apartment	1.85	0.03	1.4%
Clean Lab.	1.35	0.05	3.8%
Downstairs Shop	5.25	0.01	0.2%

From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 5 **Mercury Levels in Lab Water and Acids**



From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

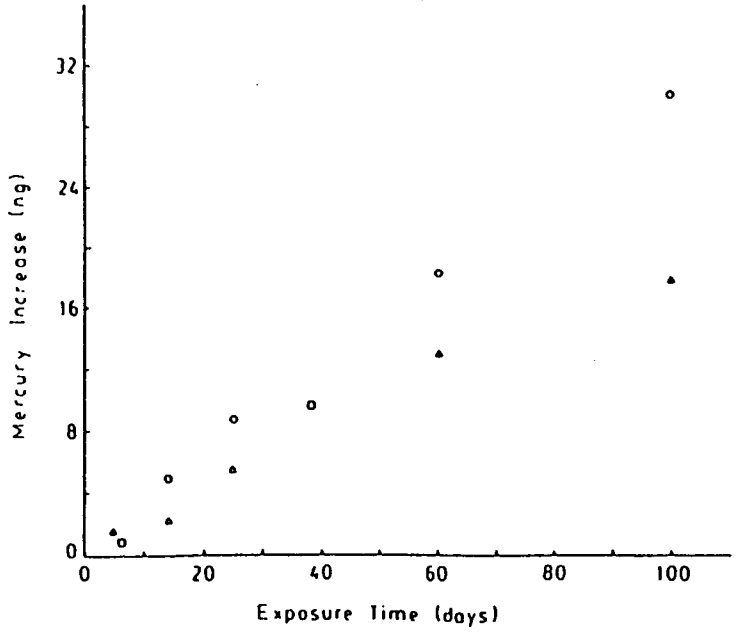
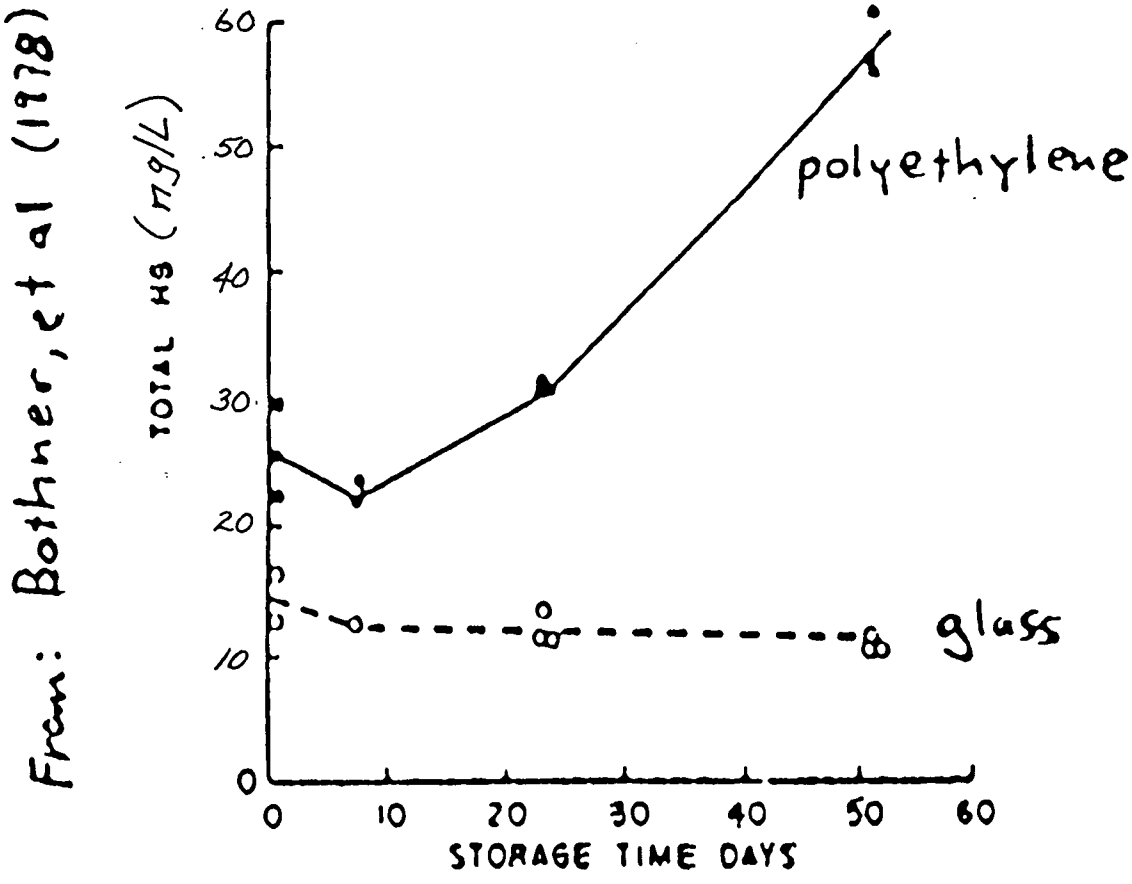


Figure 6 CONTAMINATION OF ACIDIFIED SEAWATER EXPOSED TO LAB. AIR CONTAINING APPROX. 150 ng/m3 GASEOUS Hg.

From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 7



From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 8 DUAL HG SAMPLING BURRARD INLET 91/03/21

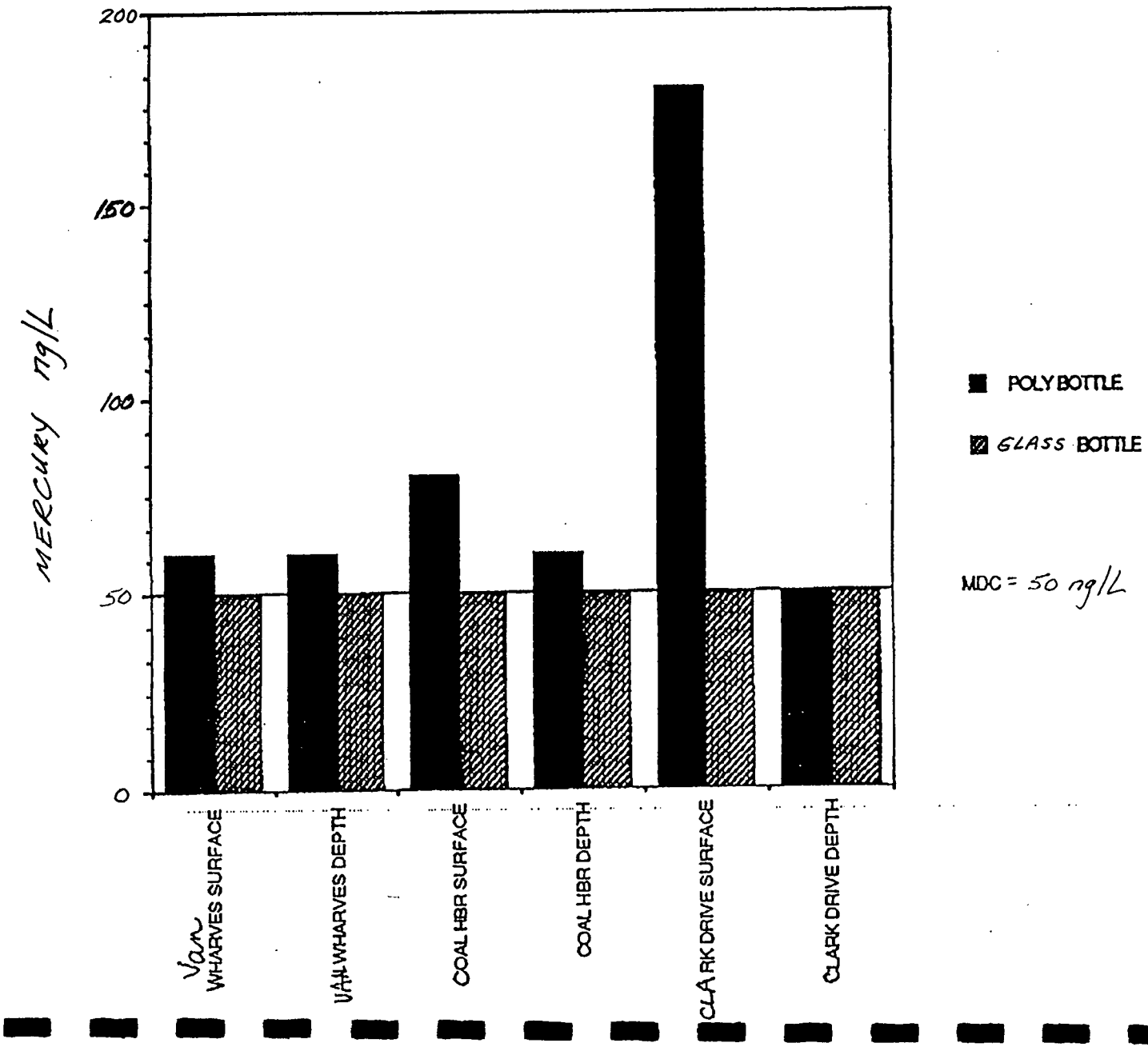


Figure 9 COST/BENEFIT ANALYSIS OF TEFLON BOTTLES (1 L bottles)

	Teflon	Glass (w/ teflon lid)
Initial cost:	$ 75.	$ 8.
initial cleaning:	$ 8.	$ 8.
number of uses:	~100	~20
initial cost·use^{-1}:	$ 0.83	$ 0.80
cost of cleaning·use^{-1}:	$ 8.	$ 8.
express shipping·use^{-1}:	$ 0.45	$ 1.80
TOTAL COST·USE^{-1}:	$ 9.28	$ 10.60
characteristics:	• unbreakable • inert/nonadsorptive • better seal • light	• breakable • strong surface adsorption • poor sealing • heavy

From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 10 EXAMPLES OF CONTAMINATION DURING SAMPLE COLLECTION

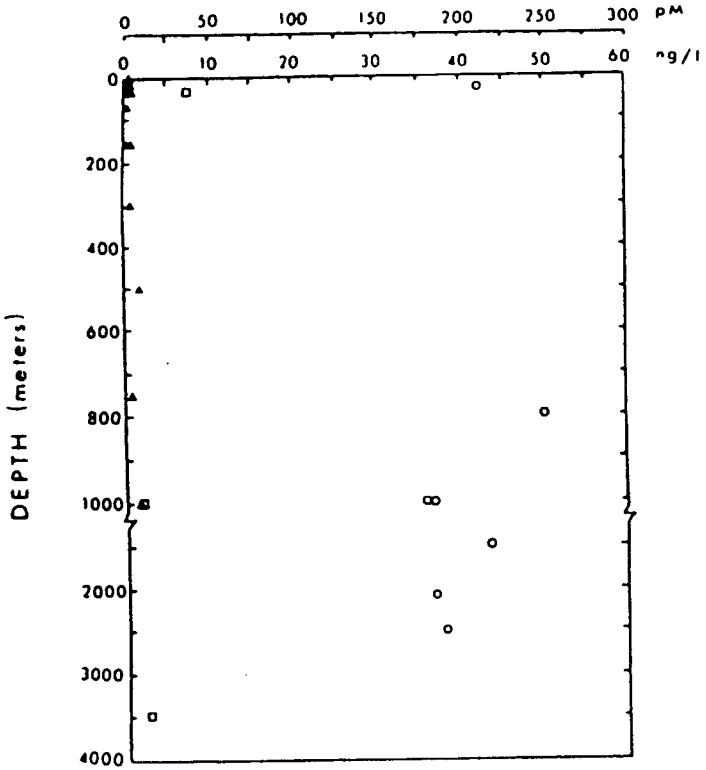


Fig. 1. Reactive Hg determinations from surface and deep waters of the northwest Atlantic (34°11'N, 66°06'W) using several different collection methods to test for contamination during sampling. R.V. *Endeavor*, 13 to 26 July 1979. □, Collections with the CIT sampler suspended at the end of the hydrowire; ○, conventional collection using a previously tested PVC sampler attached directly to the metal hydrowire; △, PVC sampler attached to a polypropylene line, either suspended below the metallic hydrographic cable or handheld for collections (at 5 and 10 m) from a rubber workboat; ▲, subsurface samples (0 m) collected directly into Teflon storage bottles from a rubber workboat.

1. REACTIVE Hg USING SEVERAL DIFFERENT COLLECTION METHOD (AFTER GILL AND FITZGERALD 1985)

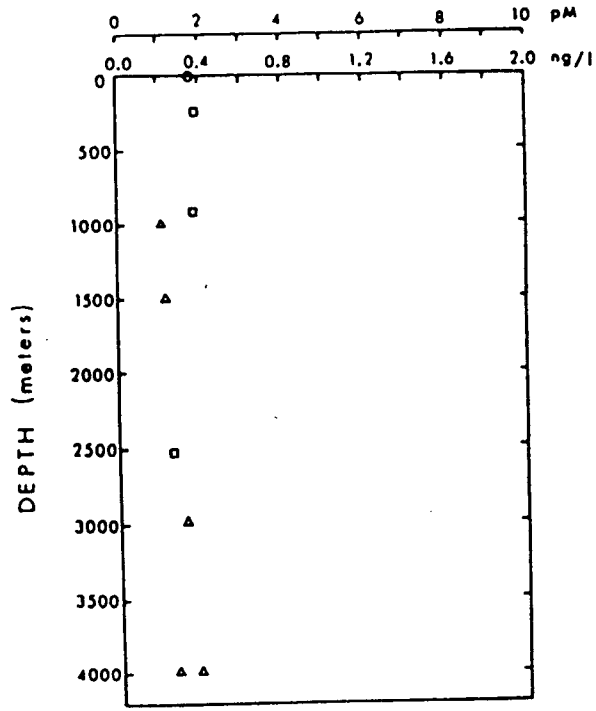
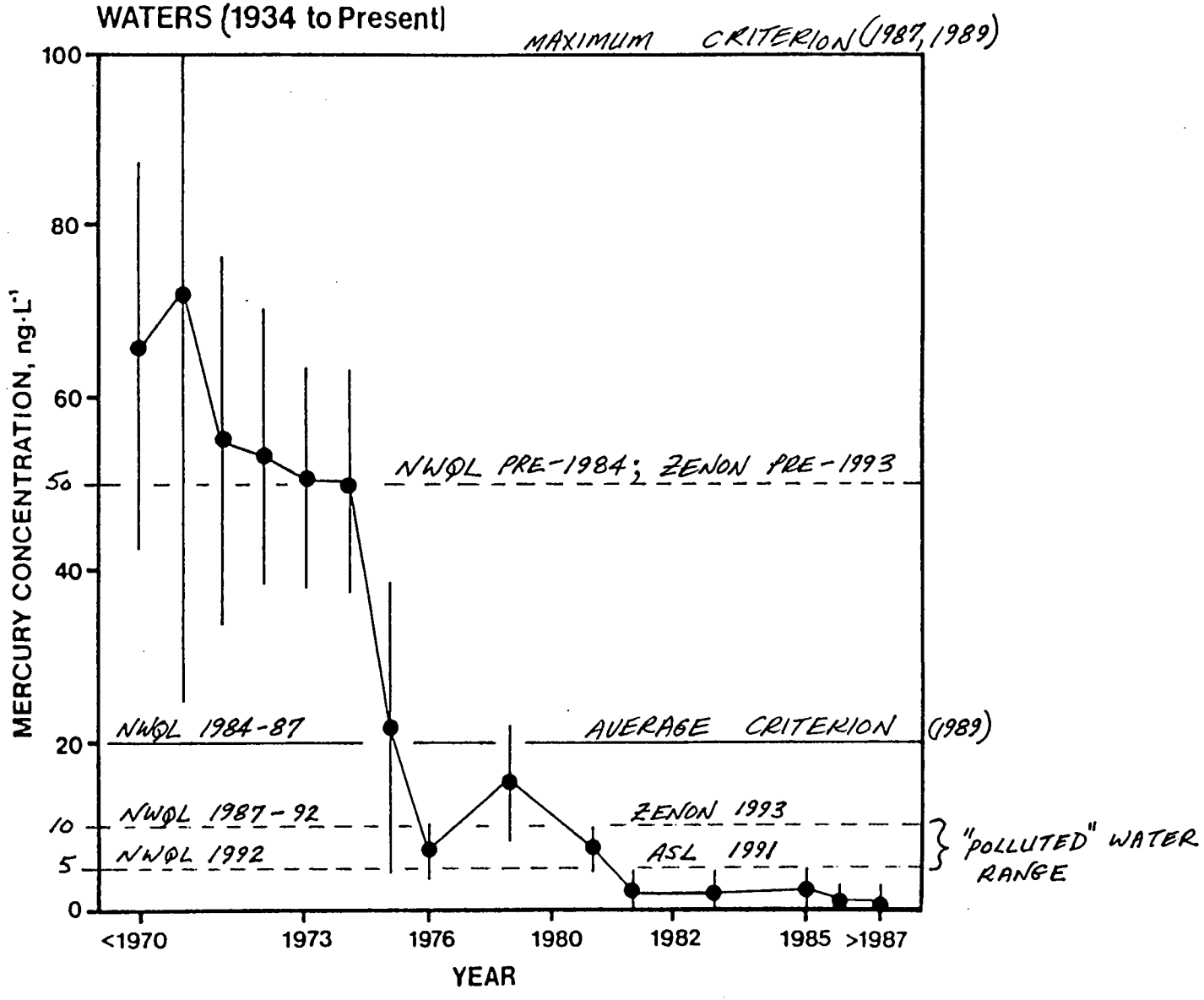


Fig. 2. Intercomparison of proven trace metal sampling methodologies for the determination of Hg at an open ocean site in the central North Pacific (14°40'N; 160°07'W), R.V. *T. G. Thompson*, 1 to 25 October 1980. Samples at depth: □, CIT deep-water common lead sampler; △, modified Go-flo bottle attached to Kevlar hydrocable. Samples of sub-surface water: ○, collected directly into Teflon storage bottles from a rubber workboat (value shown is the mean for five collections taken over a 4-day period).

2. INTERCOMPARISON OF DIFFERENT PROVEN TRACE METAL SAMPLING METHODS (AFTER GILL AND FITZ. 1985)

Figure 11 MEAN TOTAL MERCURY IN UNPOLLUTED SURFACE WATERS (1934 to Present)



From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

Figure 12

TYPICAL DETECTION LIMITS FOR MERCURY SPECIATION IN WATER

Mercury Species	Sample Size	Detection Limit $ng \bullet L^{-1}$	Typical Level in Uncontaminated Waters, $ng \bullet L^{-1}$
Total	100 mL	0.05	1.0
Acid labile	100 mL	0.002	0.05
Hg°	1,000 mL	0.0001	0.02
Particulate	On filter	~0.02	0.2
Complexed Organic	100 mL	0.08	0.8
Total methylmercury	50 mL	0.004	0.05
Dimethylmercury	1,000 mL	0.0001	<0.0001
Labile Methylmercury	50 mL	0.002	0.02
Particulate methylmercury	On filter	~0.005	0.04

From: Brooks Rand Ltd., Environmental Sciences Division. 1990. Determination of Mercury Speciation in Environmental Samples. Seminar Procceedings, November 16, 1990, Seattle, Washington.

SUSPENDED SEDIMENTS

WHOLE BOTTLE ANALYSIS

Norman L. Wade

Environment Canada

Pacific and Yukon Region

POTENTIAL SOURCES OF ERROR IN MEASUREMENT OF SUSPENDED SEDIMENTS FOR WATER QUALITY PROGRAMS

Norman L. Wade

Introduction

The measurement of suspended sediment is usually an essential component of a water quality monitoring program. High suspended sediment concentrations can be a threat to fisheries habitat and to drinking water supplies. Nutrients and a variety of toxic inorganic and organic pollutants can be transported with suspended sediments. Sediments can affected the productivity of an aquatic ecosystem and in some cases be a health concern.

Many water quality data collection programs measure non-filterable residue (NFR). These samples are not generally taken with a standard sediment sampler and usually analyzed by sub-sampling a large collection bottle. Total suspended sediment (TSS) is measured by Water Survey Canada (WSC) and the U.S. Geological Survey (USGS) using standard point or integrated depth samplers and by contrast all the material collected in the sample bottle is analyzed.

A comparison of data collected from the Stikine and Iskut Rivers (Chuchland and Schreier, 1984) showed a differance of 35 to 76% between NFR samples collected by Environment Canada and TSS collected by WSC and USGS (Table I, Fig. 1). Three hypotheses were put forward to explain these differances (Churchland and Mah Unpublished). First, that the time of day of sampling was different. This hypotheses was quickly discounted, as there was no evidence to explain that large a differance. Second, that the sample collection methods were different. Third, that the analytical procedures were different.

Sampling Methods

A likely cause of the differance between the NFR and TSS values was the sampling methods. Environment Canada's NFR samples were obtained using a peristaltic pump whereas WSC and USGS TSS samples were collected using a P-63 depth integrated sampler. It has been observed (Golterman et al., 1983; WMO, 1981; Beschta et al., 1981) that pumped samples can provide a low estimate of suspended sediment concentration, particularly when a significant proportion of the sediment is coarse, and pumping rate is not iso-kinetic.

The lower Fraser River and the Stikine River are similar in that the suspended sediment in both rivers is composed of 20 - 40% sand during freshet (IWD, 1984; Milliman, 1980). The range of suspended sediment concentrations found in the Fraser River were similar to those found in the Stikine River except that the concentrations in the Stikine River were higher during freshet. Therefore a

comparison of TSS and NFR values from the Fraser River could also apply to the Stikine River. Table II and Fig. 2. compares the means of six samples taken with a P-63 depth integrated sampler and six samples filled in rapid succession with a peristaltic pump (Churchland and Mah Unpuplished). Although the values obtained with the P-63 sampler are biased high compared to the values obtained with the peristaltic pump, they do not fully explain the differences found in the Stikine basin data.

A comparison of the means nine samples taken with a peristaltic pump and five depth integrated samples taken with a P-63 sampler on the Stikine River itself (Table III Fig. 3) shows relatively good agreement for both total concentration and particle size.

Analytical Methods

The third hypotheses to explain the difference between NFR and TSS results is the analytical method. WSC and USGS use the same analytical method in which the entire contents of a sample bottle is measured gravimetrically either by evaporation or filtration. The water quality NFR method calls for a measured aliquot of the sample to be filtered. It was suspected that, despite vigorous shaking, a representative sub-sample could not be obtained from a sample containing a high proportion of coarse sediment (Kleiber and Erlebach, 1976).

To test this hypothesis replicate samples were collected from various rivers and streams with a peristaltic pump the intake of which was one meter below the surface and pumping at the maximum rate. At each location 10 replicate samples were collected in each of the following bottle types:

1. - 250 ml. polyethylene (subsampled)
2. - 250 ml. polyethylene (whole bottle)
3. - 100 ml. polyethylene (whole bottle)
4. - 500 ml. glass (suspended sediment analysis)

The first bottle type was analyzed by the normal NFR method where a measured aliquot was drawn though a preweighed 0.45 micron filter with a vacuum aspirator. The material on the filter was then determined gravimetrically. The second bottle type was analyzed in the same manner as the first type except that the entire contents of the bottle was poured into a graduated cylinder and the volume recorded. These contents were then filtered, the bottle and the cylinder were rinsed and this rinsate was added to the filter. The material on the filter was determined gravimetrically as above. The third bottle type analyzed in an identical manner to the second only the bottle size differed. The fourth bottle type was analyzed by WSC by their filtration method.

The results of this study (Table IV, Fig. 4) show a substantially lower result for the NFR samples which were subsampled when compared to the TSS samples. The NFR samples where the whole bottle was used however show good agreement with the TSS samples.

It appears that the subsampling step can be a major source of error in the analysis of Non Filterable Residue when the concentrations are high. This low bias can also be expected to affect variables which are associated with suspended sediment and have a subsampling step, such as total metals.

Acknowledgements

This presentation was based on an unpublished paper 'Potential Sources of Error in Measurements of Suspended Sediments for Water Quality Programs' By L.M. Churchland and F.T.S. Mah.

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SUSPENDED SEDIMENT CONCENTRATIONS

COLLECTED BY DIFFERRENT AGENCIES IN THE STIKINE BASIN

DATE	LOCATION	CONCENTRATION mg/L WQB*	WRB & USGS**	% DIFF
03/06/82	Stikine above Choquette	722 ± 67	1101	66
03/06/82	Iskut below Johnson R.	303 ± 17	581	52
03/06/82	Stikine near Wrangell AK	498 ± 52	1070	47
04/06/82	Stikine above Choquette	680 ± 52	1076	63
04/06/82	Iskut below Johnson R.	276 ± 19	423	65
04/06/82	Stikine near Wrangell AK	551 ± 38	875	63
20/07/82	Stikine above Choquette	120 ± 16	341	35
20/07/82	Iskut below Johnson R.	127 ± 14	278	46
20/07/82	Stikine near Wrangell AK	125 ± 20	220	57
21/07/82	Stikine above Choquette	143 ± 11	280	51
21/07/82	Iskut below Johnson R.	152 ± 12	285	53
21/07/82	Stikine near Wrangell AK	179 ± 58	300	60
03/10/82	Iskut below Johnson R.	47 ± 5	85	55
03/10/82	Stikine near Wrangell AK	65 ± 9	155	42
04/10/82	Stikine above Choquette	46 ± 9	114	40
04/10/82	Iskut below Johnson R.	47 ± 5	67	70
04/10/82	Stikine near Wrangell AK	46 ± 6	85	54

NOTE:

* Values are means and 95% confidence limits of nine pumped samples throughout a river cross section. Samples analyzed by the non-filterable residue method.

** Values are published values derived from one to several depth integrated samples. Samples analyzed by the evaporation or filtration method. WRB sampled Stikine above Choquette and Iskut below Johnson R.; USGS sampled Stikine near Wrangell AK.

Table I

STIKINE BASIN

Nonfilterable Residue – Suspended Sediment Concentrations

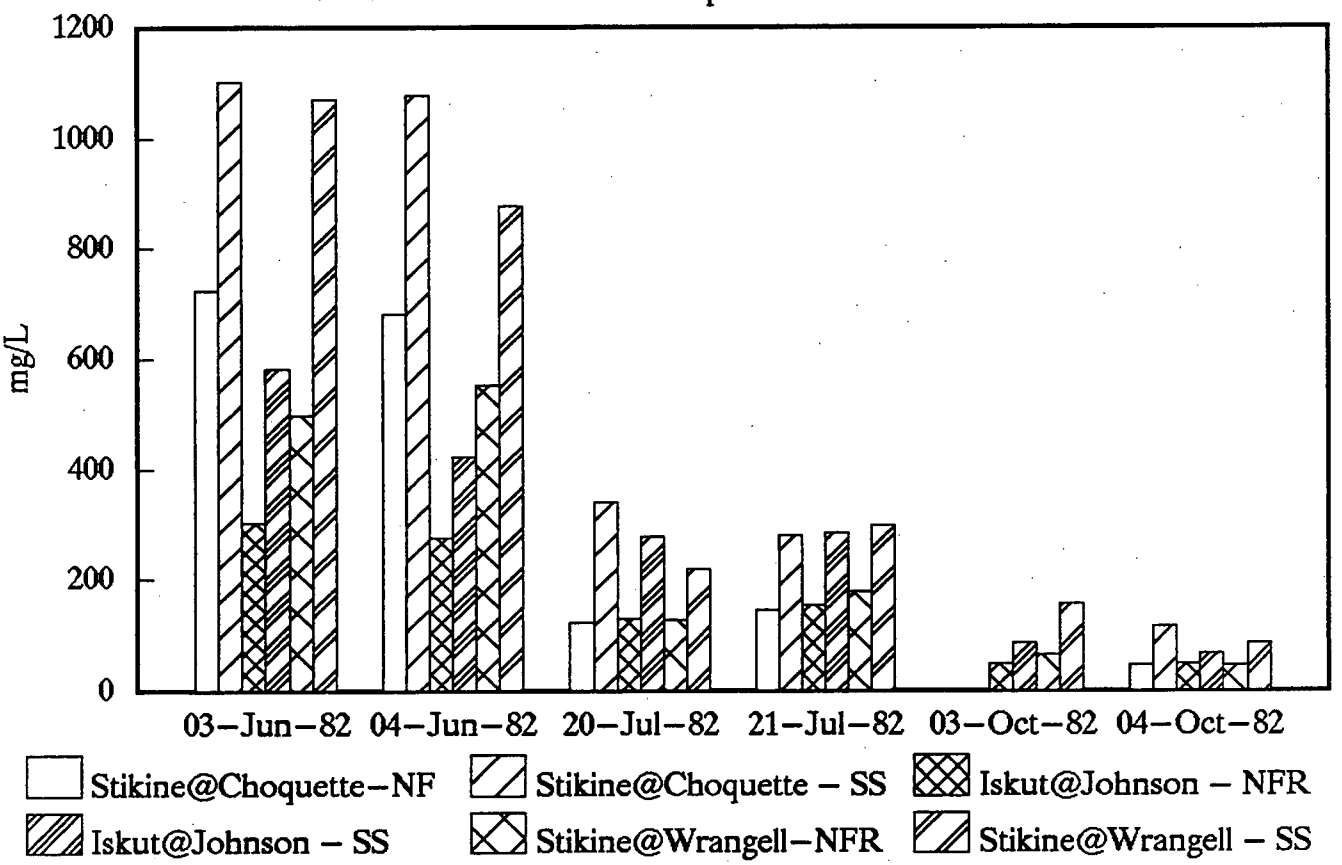

Fig. 1

SUSPENDED SEDIMENT CONCENTRATIONS

COMPARISON OF P63 SAMPLER AND PERISTALTIC PUMP IN LOWER FRASER RIVER

LOCATION	DATE	DEPTH M	Concentration mg/L PERISTALIC PUMP	Concentration mg/L P63 SAMPLER
North Arm @ Oak St. Bridge	06/05/77	1	157 ± 5	166 ± 21
North Arm @ Oak St. Bridge	06/05/77	11	180 ± 8	179 ± 17
North Arm @ Oak St. Bridge	04/07/77	5	74 ± 5	86 ± 19
Main Arm @ Tilbury Island	16/05/77	5	362 ± 24	410 ± 53
Main Stem @ New Westminster	19/04/77	10	153 ± 5	166 ± 9

NOTE:

Values are arithmetic means and 95% confidence limits of six samples

Table II

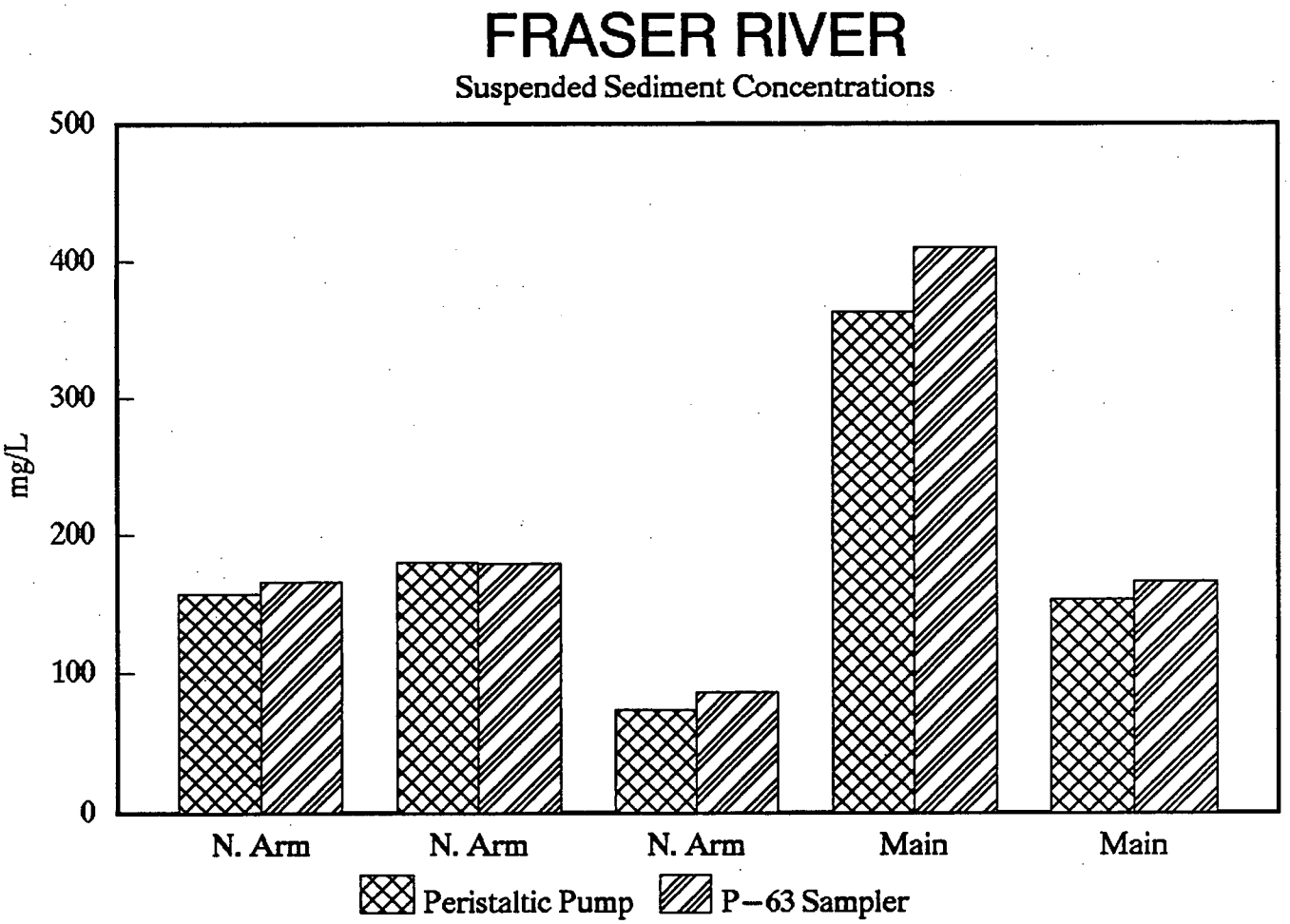
FRASER RIVER
Suspended Sediment Concentrations
500
400
300
200
100
0
mg/L
N. Arm
N. Arm
N. Arm
Main
Main
Peristaltic Pump
P−63 Sampler

Fig. 2

SUSPENDED SEDIMENT CONCENTRATION AND PARTICAL SIZE

COMPARISON OF P63 SAMPLER AND PERISTALTIC PUMP
Iskut River below Johnson River

Date	Sampling method	Suspended Sediment mg/L	% Sand	% Silt	% Clay
12/07/80	P 63*	379 ± 30	30 ± 6	41 ± 4	29 ± 7
12/07/80	Peristaltic Pump **	391 ± 78	31 ± 9	47 ± 7	22 ± 3

NOTE:

* Values are means and 95% confidence limits of five depth integrated samples across the river.

** Values are means and 95% confidence limits of mine pumped samples through a river cross section.

Table III

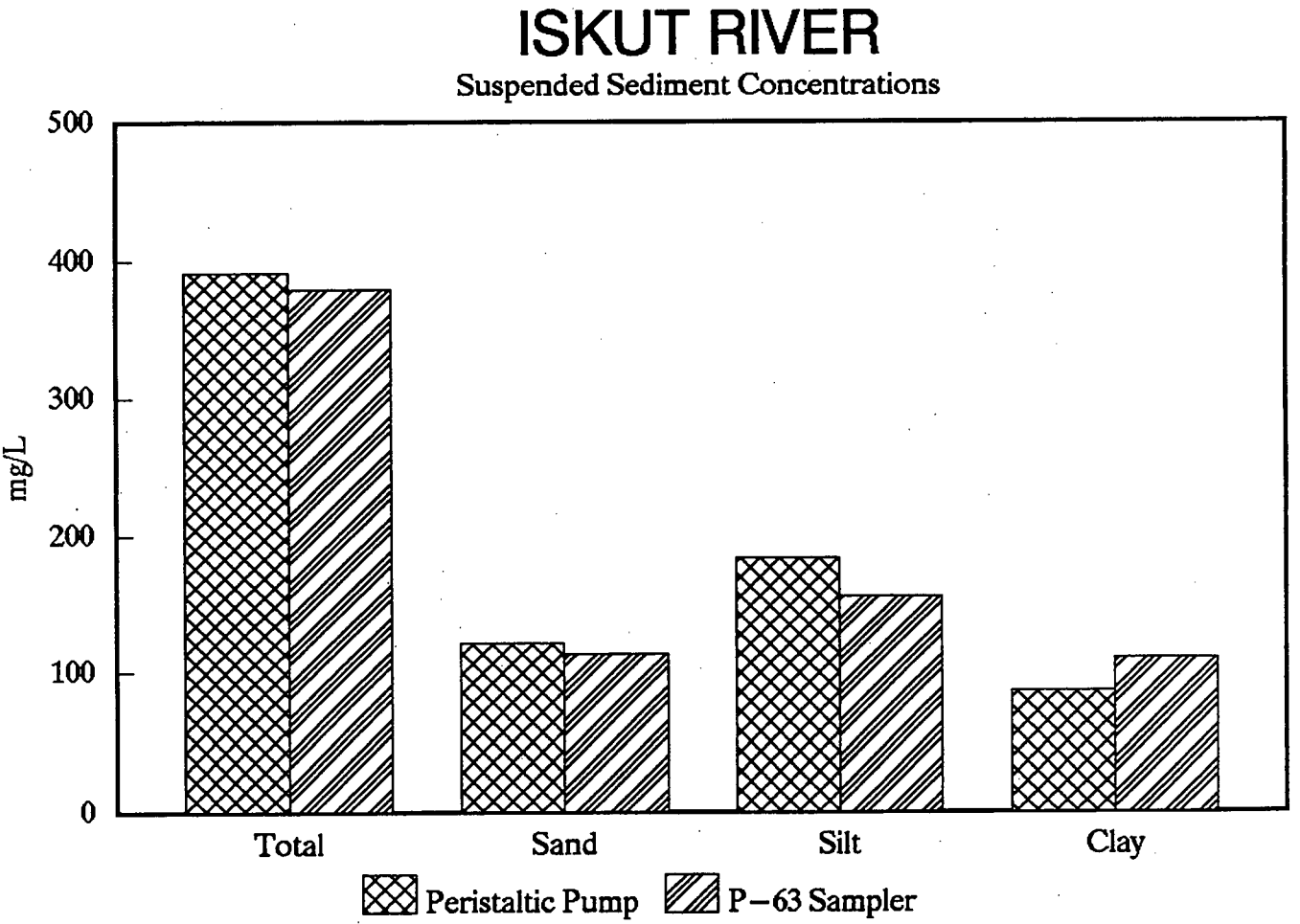
ISKUT RIVER
Suspended Sediment Concentrations
500
400
300
200
100
0
mg/L
Total
Sand
Silt
Clay
Peristaltic Pump
P−63 Sampler

Fig. 3

EFFECT OF ANALYTICAL TECHNIQUE ON CONCENTRATION OF SUSPENDED SEDIMENTS

Location	Date	Non Filterable Residue A mg/L	B mg/L	C mg/L	TSS mg/L
Liard River	16/05/84	107 ± 8	165 ± 14	172 ± 21	187 ± 10
Swift Current Creek	28/07/84	488 ± 10	561 ± 9	540 ± 15	549 ± 9
Squamish River	07/06/83	83 ± 3	137 ± 7	142 ± 9	137 ± 10
Fraser River at Mission	22/06/83	100 ± 12	157 ± 15	148 ± 17	156 ± 33
Greely Creek	29/07/84	180 ± 18	437 ± 90	455 ± 57	390 ± 46
Sumas River	16/11/83	25 ± 4	29 ± 4	35 ± 6	32 ± 1

NOTE:

Values are arithmetic means and 95% confidence limits, sample size is ten.

A is the analysis of a 100ml subsample from a 250 ml bottle.
B is the analysis of the total contents of a 250 ml bottle.
C is the analysis of the total contents of a 100 ml bottle.

Table IV

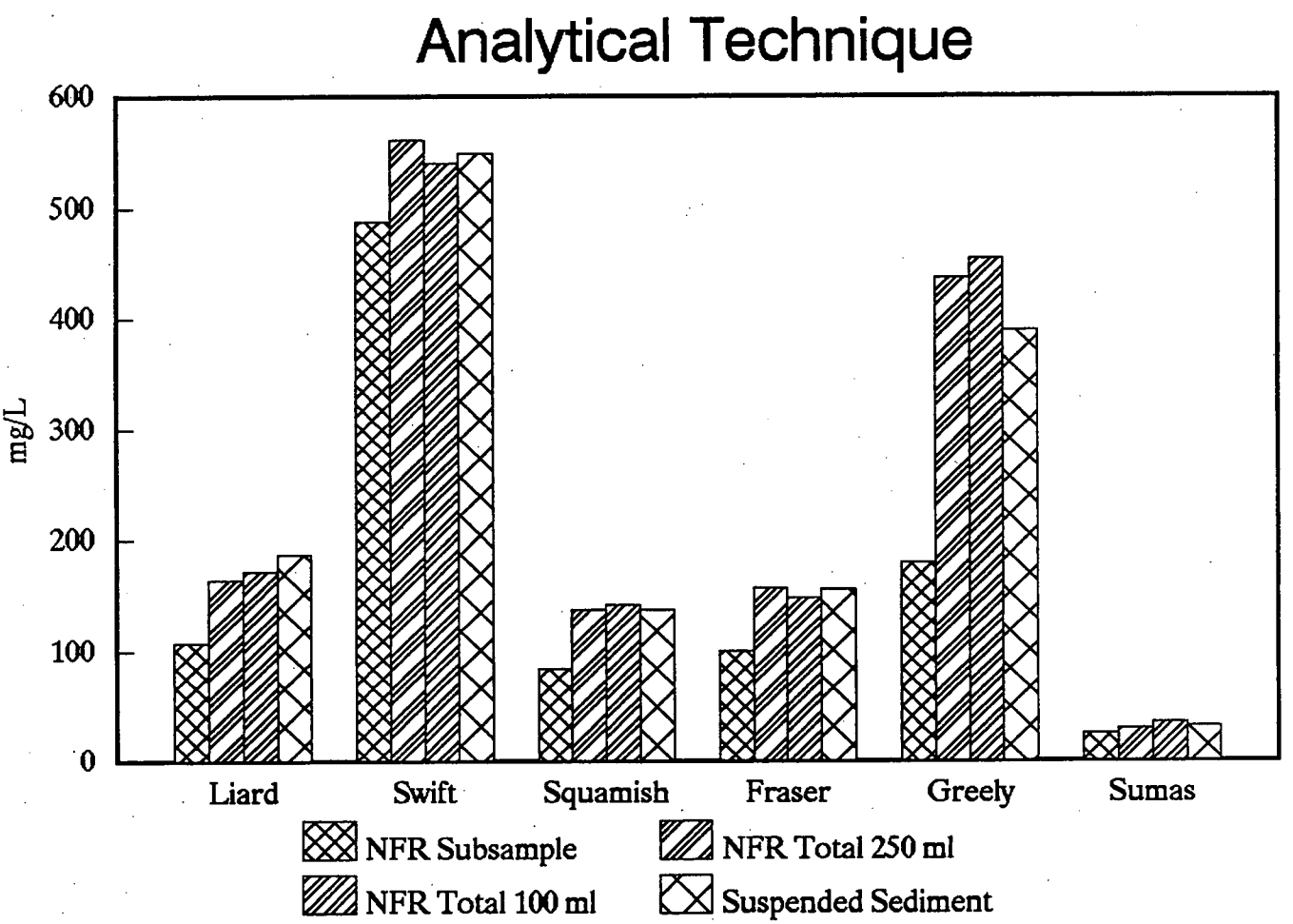
Analytical Technique
600
500
400
300
200
100
0
mg/L
Liard
Swift
Squamish
Fraser
Greely
Sumas
NFR Subsample
NFR Total 250 ml
NFR Total 100 ml
Suspended Sediment

Fig. 4

THE CHANGING FACE OF MONITORING

Jim Van Barneveld

British Columbia

Ministry of Environment, Lands, and Parks

The Changing Face of Monitoring

I have been asked to look into my crystal ball on what the future holds for monitoring. Following the detailed and precise discussions of the previous speakers I will attempt to focus your mind for a minute on the broad and nebulous.

We all have an intuitive appreciation of what we mean by monitoring. Attempting to put arbitrary limits to the concept will not serve any useful purpose and I will skip over this.

Monitoring takes place for a wide range of purposes, each with its inherent requirements for accuracy, precision and experimental design. Research, Grab sampling, Adaptive management ,Performance control/Permit monitoring, Plan implementation, Impact assessment verification, Legal enforcement monitoring, etc. illustrate the wide range of data gathered for some or other kind of monitoring purpose.

Currently in B.C. monitoring is carried out largely through individual programs, with a direct focus to serve one or several of the above purposes and some program objectives. Monitoring is often expensive , and the benefits may not readily be apparent. With increasingly greater competition for funds, the priority for monitoring is frequently viewed lower than that for other "more directly producing" activities. In recent years the cost of allowing a number of practices to proceed without adequate monitoring has become apparent. Global effects of ozone destruction and climatic warming , improper forest land use practices, contaminated sites, etc. are presenting society with mind-boggling bills for remediation if at all possible.

Public awareness of these (potentially) enormous impacts on the environment , ever increasing pressures of taxation, together with an emergence of the understanding of the links between environmental health and human welfare and prosperity are spawning new public demands on government. *Effective management* that will prevent large scale deterioration of the resource base and the environment, *efficient use of available funds and resources* without duplication to avoid waste of limited funds and *ecological relevance* of all programs and activities to ensure that the environment and human health and welfare is protected to the greatest extent possible. Putting these public demands together spells:

Integrated Ecosystem Monitoring

"Integrated" implies the pooling of expertise , knowledge and resource interests to ensure that common interests are addressed jointly, while apparent conflicts can be addressed effectively. I clearly also goes towards efficient use of financial, scientific and human resources as well as facilitating holistic and ecosystem based management.

"Ecosystem" implies that the principle, that all parts of the environment are linked to all other parts, must be fundamental to

environmental management. All known linkages between the elements of the environment must be accounted for and, as we are not likely to ever understand the full complexity of the ecosystem, provisions must be made to respond to the unknown linkages. The most up to date knowledge of ecosystem functions and processes must be applied at any time. Ecological relevance refers at once to all scales of ecological organization, local , regional and global.

It is within this market place that you must ply your trade. The type of data required may shift to easily observed data. There is not the money nor the time to undertake elaborate sampling schemes and complex laboratory measurements. At the same time the data must be directly relevant, accurate and reliable. Far greater attention must be paid to the context (ecosystem) within which measurements are being taken. The traditional "in lab" measurements may not present the ecosystem context within which effects of pollution, land-use, or life processes take place. You will need to adapt your equipment to "field" use. Typical measurements of biological activity can no longer be carried out in exotic 19th century equipment, but requires the full use of computer technology and principles of physical chemistry, electro chemistry etc. Some marvellously simple and rugged electrodes and electrochemical probes have been developed.This combined with computer technology allows for the measurement and data compilation of the principal factor (ex chlorophyll fluorescence to measure photosynthetic activity) as well as some of the characteristics of the environment within which these measurements will be taken. I had the good fortune to observe Bill Gensler of U.of Arizona, who has developed a rugged outdoors data acquisition pod that offers 44 data input channels. The probe for measuring oxygen (in plant tissue, in water, or wherever) consists of simple piece of titanium wire. No moving parts, no material transfer, no wear.The 44 channels provide enough replication to allow for the loss of some of the measuring probes without loosing the monitoring. The pod has now incorporated a satellite link and is capable of providing ongoing real time monitoring of 44 measurements from anywhere in the world.The cost of this pod appear to be well in line and is well below the cost of travel, person time etc. If the monitoring is warranted, this is the way to proceed.
The new marketplace for environmental monitoring offers exciting opportunities for research and technology. Classical laboratory analyses will continue to be with us but at a far more limited scale and with far greater technological sophistication.

There, now you heard it from someone else. I hope this crystal ball gazing will give you some feeling for where I think monitoring is heading, and that it will give you the inspiration to lead the pack.I may be out to lunch, but if it makes you take another look at your functions I have been successful in this presentation.
Jim van Barneveld
22/2/94

CLOSING REMARKS

Paul H. Whitfield

Environment Canada

Pacific and Yukon Region

Workshop Summary

Paul Whitfield

On behalf my colleagues I would like to express our appreciation for attending the workshop. Reflecting on the past two days, it is apparent that quality assurance is a team effort, and a shared problem. Data in the 1990's is a shared corporate resource, and it is our common responsibility to ensure that this resource has lasting value. We have heard and discussed a wide range of quality assurance; these can be grouped into four general areas. First, there are the topics which are quality assurance structures - MDC's, validation, standards, and the integrate quality assurance model. Second, there are the topics of process - sampling methods, samples in transit, sampling organics. Third, there are the topics which deal with details - pH measurements, mercury contamination, and sediment. Fourth, there are the topics of the future - ecosystem monitoring, biological measures. This brief listing conveys the range of complexities associated with good quality assurance - we must be concerned with the structures, the process, the details, and the future needs for quality assurance. This workshop has covered this spectrum; but we must recognize that it has not exhausted any of these topics.

The workshop provided an opportunity for us to meet and open a dialogue, and continue the discussions which are essential to cooperation and collaboration. It was the intention of the Coordinating Committee that this workshop would promote the communication on the topic of quality assurance. Workshops of this type are an important vehicle for communicating each of our findings, ideas, and problems. None of our agencies has the resources to resolve all of the quality assurance issues which it faces. In my opinion, the future of quality assurance focuses on achieving personal commitment to producing good data, while recognising that these data and an important corporate resource, and a significant corporate investment. I hope that each of the objectives you had in attending this workshop were met over the past two days.

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photo by Ian McLaurin
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