METHODOLOGY AND QUALITY ASSURANCE FOR NUTRIENT MEASUREMENTS BY NOAA: CURRENT STATUS AND RECOMMENDATIONS FOR THE FUTURE

A Report Resulting From a Technical Working Group Meeting in Miami, Florida, December 8-9, 1983

by

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SUMMARY

A technical working group's analysis of 13 quality assurance reports, submitted by NOAA-supported nutrient laboratories, suggests that NOAA is using state-of-the-art methodology to produce high-quality nutrient measurements for marine and Great Lakes samples. Quality control practices of most of these laboratories compare favorably with those used by other investigators in the field. Examples of good quality assurance practices reported were: the use of daily calibration curves and blank determinations, minimization of contamination and sample storage problems, use of standard reference materials when feasible, and adequate sample and analysis replication. Quality assessment (i.e. verification and documentation of quality control) was less adequate than were the quality control measures. Precision was often not adequately defined in the reports. Blind standards or standard addition techniques, to check accuracy and precision, were not used as often as desirable. Several laboratories took part in interlaboratory comparisons but not as often nor for as many nutrients as optimum, in part because some nutrient forms are not stable during prolonged sample storage.

The working group's recommendations for the future are:

To NOAA Management:

1. Recognize the high cost of adequate quality assurance programs.
2. Encourage technical project officers to include a strong quality assurance component in outside NOAA contracts for nutrient analysis.
3. Improve NOAA quality assurance guidelines.
4. Provide information on availability of standard reference materials.
5. Implement preparation of new standard reference materials.
6. Encourage interlaboratory comparisons among groups with similar samples, but do not implement a NOAA-wide intercalibration program.
7. Periodically review analytical and quality-assurance procedures for nutrient analysis in NOAA and NOAA-supported laboratories.
8. Be specific on requested details if future quality assurance questionnaires are used.
9. Periodically distribute nutrient analysis information among scientists within and supported by NOAA.

To NOAA and NOAA-Funded Laboratories:

1. Consider quality assurance guidelines in planning research and monitoring programs.
2. Calibrate laboratory instruments and prepare standards at specified intervals.

3. Analyze standards in the same or similar matrices as samples.

4. Use standard reference materials at regular intervals.

5. Consider thawing as well as freezing conditions when samples are frozen before analysis.

6. Check multiple-nutrient standard solutions for cross interferences.

7. Increase the use of blind standards.

8. Report low-level estimates to prevent bias in statistical examination of results.

9. Include quality assurance results in research or data documentation.

INTRODUCTION

After the formation of the NOAA Quality Assurance Program for Marine Environmental Measurements, all laboratories doing nutrient analysis within or supported by NOAA were requested to submit a report on their quality assurance practices. Information requested for these reports included: types of nutrients measured, sample matrices analyzed, rationale for analysis, chemical and quality-assurance methodology, calibration and data-handling approaches, and modes of publication of results. Quality assurance reports, in varying detail, were received from 13 laboratories (see last section of report for list of participants). A technical group of specialists from within and outside of NOAA was assembled and asked to review and assess these reports and make recommendations for future action to NOAA.

A meeting of this technical working group was held December 8-9, 1983, at the NOAA Atlantic Oceanographic and Meteorological Laboratory in Miami, Florida. Specific purposes of this meeting were: 1) To assess the current status of NOAA quality assurance for inorganic nutrient measurements, 2) to document current methods used in NOAA funded research and monitoring programs, and 3) to recommend actions to correct defficiencies and document the accuracy and comparability of future NOAA data. Results and conclusions of the meeting are summarized below:

CURRENT STATUS OF NUTRIENT ANALYSIS BY NOAA FUNDED LABORATORIES

Methodology

Most reports received from the various laboratories within and supported by NOAA were of high quality and indicated that methodology used by these groups to measure nutrients is at the state-of-the-art level. (In contrast to the majority, reports of two NOAA-funded laboratories provided no detail about quality assurance practices, but only indicated method references; these reports were of little value to the working group's evaluation.) Chemical methods to measure respective nutrients were generally consistent among the

various laboratories, and the working group felt that NOAA laboratories compare favorably with other scientific groups that measure nutrients in aquatic systems. However, the documentation of nutrient methodology was diverse and somewhat difficult to decipher in the responses, mainly because of the large number of published and unpublished modifications of standard recognized procedures. To clarify this problem, the working group categorized the reported methodology according to nutrient form, chemical principle of analysis, primary and secondary reference publications, sample matrix, and respective NOAA users (Table 1). This table provides a summary of current nutrient methodologies in NOAA and provides access to the various procedures and modifications mentioned.

Quality Assurance

Quality assurance can be subdivided into quality control and quality assessment categories. Quality control includes procedures used to produce measurements of desired quality, whereas quality assessment involves verification and documentation of quality control measures. To evaluate the effectiveness of NOAA quality assurance in an "objective" manner, an evaluation sheet was prepared and used to review the reports submitted by NOAA and NOAA-supported laboratories (Figure 1). Evaluation of the reports by this mechanism indicated that NOAA laboratories conducting nutrient analysis were generally doing an adequate, or better, job in implementing quality control measures, but should improve their quality assessment practices. Reporting was not uniform among the laboratories and documentation of quality control measures was often not available.

Specific working group comments on reported quality control and assessment measures are summarized below.

Quality Control Measures. The working group concluded that NOAA laboratories were functioning well in the following areas:

1. Use of daily or more frequent calibration curves and appropriate reagent blanks. Virtually all respondents indicated that frequent calibration curves and blanks constitute an important aspect of their analysis procedures. In addition, many responding laboratories routinely included internal standards within their sample manipulations. Some respondents routinely bracket sample runs with calibration curves.

2. Minimization of contamination and sample storage problems. Responding laboratories generally took appropriate precautions to minimize sample contamination, both in the field and in the laboratory. Sample bottle washing and rinsing and proper handling of other necessary glassware were indicated in most responses. One aspect ignored in several reports was the need to preclean or rinse filters before sample filtrations. Hopefully, this was an omission in reporting rather than in practice. Sample storage problems were recognized and appropriately compensated for by most respondents. Varying opinions were expressed by some about the best storage procedures for different nutrients.

3. Use of standard reference materials. Standard reference materials were used to some extent by some laboratories. However, the frequency of analysis varied widely. Many groups stressed that available standard reference materials are inadequate for some nutrients. Available reference materials tend to be too concentrated, supplied in an inappropriate matrix, or are unstable at appropriate concentrations for some nutrient forms. Standard reference materials supplied by the U.S. Environmental Protection Agency are commonly used in fresh water analysis.

4. Sample and analysis replication. The importance of collecting samples in replicate and of doing replicate analyses on given samples was recognized by most respondents. Most groups incorporated some replication in their designs for sampling and analysis, but the frequency of replication varied greatly. Some groups duplicated analyses on only suspect samples, whereas others replicated analyses either on all samples or on certain preselected ones. Laboratories involved with monitoring tended to replicate a lower percentage of samples than did those emphasizing experimental studies, but replication plans for both were generally designed for good quality control.

Quality Assessment. The working group concluded that the following aspects of quality assurance (mostly assessment) should be improved:

1. Definition of precision. Although precision was generally evaluated and reported for each method by the respondents, the units of precision were often missing. Without mention or definition of units, the reader cannot accurately compare the precisions of different methods. In addition, some respondents did not distinguish between precision levels of standards and samples.

2. Use of blind standards and/or standard addition techniques. With only a few exceptions, use of alternate methods or blind standards to demonstrate accuracy were not used by responding laboratories. In some instances, alternate methods of analysis were used, but this was not routine. Standard addition approaches, to assess accuracy of techniques and examine the presence and magnitude of sample matrix interferences, were not widely used.

3. Minimal participation in interlaboratory comparisons. Round-robin analysis of split samples is another important mechanism to assess accuracy and find hidden problems in analysis. Intercalibration exercises are useful for assessing differences in instrumental and/or laboratory techniques as well as for detecting errors in analysis. However, the responses indicated that only about one-half of the laboratories participated regularly in such comparisons. Some laboratories participated only for a small number of nutrients and a few laboratories apparently never had participated. Laboratories involved with monitoring tended to be stronger in this effort then experimental laboratories. The working group recognizes that such comparisons must be carried out with care because problems such as sample storage and stability of low-level samples must be taken into consideration for meaningful results. The

best way to do intercalibration studies is for the analyst to do the measurements on the same research vessel or laboratory or with a neighboring laboratory at approximately the same time.

4. Other factors. Other possible areas of sampling and analysis (discussed by the working group but not included in the submitted reports) that may affect data quality include: consideration of sample matrix, attention to proper handling of samples during freezing and thawing periods, and analysis of samples from polluted areas that may have unusual pHs or concentrations of interfering substances such as sulfide, arsenate, or other materials. Salinity is an important matrix characteristic that must be considered in estuarine studies where samples have varying salinities.

General Observations of Working Group

Guidelines for documentation. One problem associated with data sets and reports is that essential quality assurance information is often not adequately documented. For example, standardizations, estimates of precision, and limits of detection for particular analyses are often not part of data reports. Such quality assurance information is necessary for the interpretation and assessment of the data by present and future users. A potential cause of the lack of quality assurance information is the absence of guidelines for such documentation. Formats for reporting quality assurance parameters are not standardized in NOAA laboratories. The need for this information has not been sufficiently stressed nor has the inclusion of such information with data reports been emphasized.

Importance of Personnel. The employment of competent and dedicated personnel was recognized as one of the most important aspects of quality assurance. Obviously, data are only as good as the analyst, and personnel with adequate training in, and awareness of, good quality assurance practices are essential to implement a successful program. Laboratories with frequent turnover of personnel may sometimes have more problems obtaining consistent and accurate results than those having long personnel commitments. Thorough personnel training, although expensive, is an extremely important part of a good quality assurance program. The availability of carefully documented laboratory methods and good quality control practices during personnel changes is necessary to preserve continuity within the laboratory and assure good quality data on a long-term basis.

Experimental Design. Current NOAA research involves the study of a variety of natural systems, including lakes, rivers, estuaries, and open ocean areas, and involves a wide range of matrices from surface waters to sediments and pore waters. Sampling location and frequency must be carefully planned to address the large variations occurring in natural systems on both temporal and spatial scales, and experimental design is an important component of quality assurance. While all aspects of the sampling program should be scrutinized at the initiation of a project, it is recognized that some portions are most properly addressed as part of the scientific question (e.g., patchiness). Other aspects (e.g., appropriate techniques and equipment and sample-bottle contamination) are more strictly quality assurance questions. A determination must

be made of how well the project addresses the questions asked, and of how representative it is of the natural processes being described. Quality assurance involves not only the accuracy and precision of the data, but also the quality of the overall product, from experimental design and sampling to final analysis and presentation of results.

RECOMMENDATIONS FOR FUTURE QUALITY ASSURANCE ACTIONS FOR NUTRIENT ANALYSIS IN NOAA

Recommendations to NOAA Management:

1. Recognize the high cost of adequate quality assurance programs. Quality assurance is an essential part of successful environmental measurement programs, but is expensive to implement. For monitoring projects, the working group believes that an adequate quality assurance program will require at least 10 to 15% of the total project cost. The cost will be greater if new method development is involved.

2. Implement a strong quality assurance component into outside contracts awarded by NOAA to provide nutrient data. This precaution is needed to assure that data obtained from potential bidders (who in some cases are inexperienced in nutrient analysis) will be accurate and comparable to that obtained by competent laboratories. NOAA should consider reserving some quality assurance funds to improve quality assurance work in future outside contracts. When proposals for work are solicited by NOAA, credit should be given to contractors having a quality assurance/quality control program and using state-of-the-art analytical methods. Quality of analysis, rather than only the lowest bid, should be a critical criteria for awarding contracts.

3. Improve quality assurance guidelines. NOAA should develop better and more precise quidelines and mechanisms for achieving and documenting adequate quality assurance both in contracted work and in-house research. Guidelines should be included with requests for proposals (RFPs) and/or contract specifications. In particular, the quality assurance guidelines should require that contractors define such terms as precision and detection limits and provide some quality control results (such as replicate values, performance on standard reference materials and/or blind standards) in project reports. The working group recognizes that the diversity of monitoring and research conducted or funded by NOAA precludes establishment of inflexible quality assurance requirements, and we specifically recommend against establishing "onerous and bureaucratic" requirements. Although specific details of quality assurance requirements should be left to the discretion of the contract officer, a set of guidelines would help him/her select appropriate criteria.

4. Provide information on availability of standard reference materials. Information on sources of standard reference materials for all nutrient forms in fresh water, sea water, and sediments should be assembled and disseminated to NOAA scientists and contractors. Some known and potential sources of references materials are: U.S.

Environmental Protection Agency, Environmental Research Laboratory, Cincinnati, Ohio; Sagami Chemical Center, Japan; Sigma Chemical Corp., St. Louis, Missouri; U.S. National Bureau of Standards, Gaithersburg, Maryland; National Research Council of Canada, Ottawa; and various European and international organizations such as UNESCO, OEDC, and NATO.

5. Implement preparation of new standard reference materials. If certified reference standards are not available for all nutrient forms and matrices, efforts should be made to have such reference materials made if feasible. Ideally, the National Bureau of Standards should be requested to undertake this task.

6. Encourage interlaboratory comparisons. The working group strongly encourages informal or formal interlaboratory comparisons of nutrient measurements. Selection of the best mode for these intercalibrations should be done, however, the laboratory level based on similarity of analytical requirements and sample matrices rather than on governmental organization structure. For example, the working group does not encourage a NOAA-wide intercalibration of samples, but would encourage neighboring laboratories within and outside of NOAA to participate in intercalibration measurements of nutrients on split samples or standard reference materials.

7. NOAA should periodically review analytical and quality-assurance procedures for nutrient analysis. A nutrient group should meet again in 2-3 years to examine and evaluate nutrient-measurement techniques. In addition to considering procedures for inorganic nutrients considered here, methods for particulate and dissolved organic nutrients and for other related water quality parameters (e.g. dissolved oxygen, chlorophyll, pH) should be evaluated.

8. Design specific questionnaires for future quality assurance surveys. Future questionnaires on quality assurance, if used, should be specific about responses needed from participating laboratories. The nature and level of detail needed should be specified clearly so responses will be uniform among the groups.

9. Periodically distribute nutrient analysis information among scientists within or supported by NOAA. A list containing the names of investigators, study areas, sample matrices, and nutrients measured should be sent to members of the "NOAA nutrient network" on a regular basis.

Specific Quality Assurance Recommendations and Suggestions for NOAA and NOAA-Funded Laboratories:

1. Consider quality assurance guidelines in the design and implementation of experimental and monitoring programs. "Guidelines for data acquisition and data quality evaluation in environmental chemistry", Anal. Chem. 52:2242-2249 (1980), and "Principles of environmental analysis", Anal. Chem. 55:2210-2218 (1983), should be used as guides for quality assurance in programs analyzing field of laboratory samples.

Additionally, "Reporting low level data" from the Quality Control Handbook for Pilot Watershed Studies, PLUARG, International Joint Commission, Windsor, Ontario, Canada, March 1980 (Appendix I) should be examined as a guide for reporting data near or below the limits of detection. See also "Standard practice for intralaboratory quality control procedures and a discussion on reporting low-level data, ASTM Designation D 4210-83", Annual Book of the ASTM Standards 11.01:7-16 (1983)

2. Calibrate laboratory instrumentation and prepare standards at specified time intervals. Balances should be calibrated, new standards prepared, and standard linearity checks (of colorimeter and recorder responses) checked regularly as part of standard operational procedures for good quality assurance.

3. Run standards in the same or similar matrices as samples. The matrix of the sample can affect nutrient measurement results. For example, salt composition and concentration can affect results of some variations of the phenol-hypochlorite procedure for ammonium and the stannous chloride method for soluble reactive phosphorus.

4. Use standard reference materials at regular intervals to assess accuracy of techniques. If standard references are not available in the appropriate concentration or matrix, an interim alternative is to spike low-level samples with concentrated standard solutions prepared on deionized water. Spiking a small volume of concentrated standard into a low-nutrient sample provides a "fresh reference material" having the appropriate matrix for analysis.

5. Consider thawing conditions when samples are preserved by freezing. Thawing rate, as well as freezing rate, is an important factor to consider, particularly for silica analysis where the apparent silica concentration depends on the time interval between thawing and analysis.

6. Check multiple-nutrient standard solutions for cross interferences. Components of multi-nutrient calibration standards, prepared for automated multi-nutrient analysis, should be examined for purity. For example, phosphate is a frequent contaminant of nitrate salts, and in a mixed standard this could lead to a systematic error in phosphate analyses.

7. Increase use of blind standards. Use of blind standard provides an unbiased estimate of precision and accuracy obtained by the analyst making nutrient measurements.

8. Report low-level estimates (with qualifications). When reporting data in scientific publications and/or archiving data in computer files (e.g. long-term monitoring), the working group suggests reporting values actually calculated (including zero or negative values resulting from blank subtraction) along with the appropriate code or superscript indicating if the value is below the limit of detection (e.g. 3 times the standard deviation of the blank) or below the limit of quantification (e.g. 10 times the standard deviation of the blank) (see Appendix 1).

Reporting "best estimates" tends to prevent bias in statistical handling the results.

9. Include quality assurance results in research or data documentation. Extensive quality assurance information is sometimes excluded from refereed journal articles to save printing space, but should be included in abbreviated form, or referenced, for potential users of the data. More extensive information should be put on record in data reports and computer files.

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TABLE 1

Methods Documentation for Nutrient Analysis for NOAA

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Nitrogen				
Ammonium	Manual Method:			
	The water is treated in an alkaline citrate medium with sodium hypochlorite and phenol in presence of sodium nitroprusside which acts as a catalyzer. The blue indophenol formed with ammonia is measured at 640 nm.	Solorzano, 1969	U. of Delaware	Estuarine, 0-30°/oo
			SUNY, Stony Brook	Estuarine, 0-20°/oo and pore waters
			U. of Rhode Island	Estuarine, 0-33°/oo
			Case Western Reserve	Freshwater and pore waters
	Similar to the Solorzano technique except that sodium dichloroisocyanurate has been substituted for commercial hypochlorite solution (Chlorox) as an alternative hypochlorite donator.	Grasshoff, 1976	U. of Georgia	Estuarine and pore waters
	Similar to Grasshoff except that a UV light is also used to enhance color development.	Liddicoat et al., 1975	U. of Delaware (without UV) Treatment but with 35°C water bath	Estuarine, 0-30°/oo
			NOAA/Sandy Hook (semi-automated procedure) reagents added manually	Estuarine, 0-35°/oo

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Ammonium (Continued)		Standard Methods, 15th ed., 1980	Old Dominion Univ.	?
	Automated Methods:	Koroleff, 1969, with modifications by Slawyk and MacIsaac, 1972; Patton and Grouch, 1977	Brookhaven Nat'l. Laboratory	Estuarine, 0-35°/oo and pore waters
	This is a fluorometric technique. Ammonium is separated from amino acids by chromatography and the fluorescent product resulting from the reaction of ammonium with O-phthalaldehyde (OPA) is measured.	Gardner, 1978; Gardner and Malczyk, 1983	NOAA Great Lakes	Freshwater
	Similar to Solorzano except that the ratio of sodium citrate to sodium hydroxide used in the citrate buffer has been changed.	Koroleff, 1969	U. of Michigan	Freshwater
	Similar to Koroleff with modifications from Harwood and Huyser, 1970.	Davis and Simmons, 1979	U. of Michigan	Freshwater

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Ammonia (Continued)	The automated procedure for the determination of ammonia utilizes the Berthelot Reaction, in which the formation of a blue colored compound believed to be closely related to indophenol occurs when the solution of an ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite. A solution of potassium sodium tartrate and sodium citrate is added to the sample stream to eliminate the precipitation of the hydroxides of calcium and magnesium. The blue colored reaction is measured at 630 nm.	Technicon AAII, 1978 (Method No. 154-71W/B)	NOAA/AOML	Estuarine, 10-35°/oo
			Ohio State Univ.	Freshwater
Nitrate	The procedure for the determination of nitrate and nitrite is based on the reduction of nitrate to nitrite by a copper-cadmium reductor column. The nitrite ion is subsequently reacted with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-Naphthylethylene-diamene to form a reddish-purple Azo dye. Absorbance is then measured at 550 nm.	Armstrong et al., 1967		
		Wood et al., 1967	NOAA/AOML	Estuarine, 10-35°/oo
			Ohio State Univ.	Freshwater
			U. of Rhode Island	Estuarine, 0-33°/oo
			U. of Delaware	Estuarine, 0-30°/oo
		Technicon AAII, 1979 (Method No. 158-71W/B)		

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Nitrate (Continued)		Technicon method as modified by Gardner and Malczyk, 1983, for discrete injection segmented flow analysis.	NOAA Great Lakes	Freshwater
	Same as above with modifications to the cadmium reduction column.	Armstrong et al., 1967, as modified by Whitledge et al., 1981a	Brookhaven Nat'l. Laboratory	Estuarine, 0-35°/oo and pore waters
			SUNY, Stony Brook	Estuarine, 0-20°/oo
		Armstrong et al., 1967; Wood et. al., 1967, with modifications from Grasshoff, 1969	NOAA/Sandy Hook	Estuarine
	As in Wood et al., 1967, with buffered ammonium chloride.	Grasshoff, 1970, with modifications from Grasshoff, 1976	U. of Georgia	Estuarine
		Technicon AAII with EPA Method 353.2	Case Western Reserve	Freshwater
		Wood et al., 1967, with modifications by Davis and Simmons, 1979	U. of Michigan	Freshwater
		Standard Methods, 1975, 14th ed.	Old Dominion Univ.	?

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Nitrite	Nitrite analysis (Bendschneider and Robinson, 1952) in seawater is performed identically to that for nitrate omitting only the reduction step.			
Dissolved Organic Nitrogen	(The following responses for dissolved organic nitrogen were received but were not specifically requested in the questionnaire.)			
	UV light is used to oxidize the nitrogen-containing compounds to nitrate which then is analyzed using automated nitrate techniques described above.	Armstrong et al., 1966 Armstrong and Tibbits, 1968 Whitledge, 1981b	Brookhaven Nat'l. Laboratory	Estuarine, 0-35°/oo
	Organic nitrogen is oxidized to nitrate with potassium persulfate in an alkaline medium. The resultant nitrate is measured using techniques described above.	Solorzano and Sharp, 1980a	U. of Delaware U. of Rhode Island	Estuarine, 0-30°/oo Estuarine, 0-33°/oo
	Wet oxidation with persulfate as described in Koroleff, 1969	Grasshoff, 1976	U. of Georgia	Estuarine
	?	Total Kjeldahl nitrogen (EPA method 420B)	Old Dominion Univ.	?

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Particulate Nitrogen	(The following responses for particulate nitrogen were received but were not specifically requested in the questionnaire.)			
		Perkin-Elmer 240C CHN Analyzer	U. of Georgia	Estuarine
		?	SUNY, Stony Brook	Estuarine
		Hewlett-Packard CHN Analyzer	U. of Delaware	Estuarine
		Carlo Erba Model 1106, CHN Analyzer	U. of Rhode Island	Estuarine
			NOAA/Great Lakes	Freshwater
Urea	(The following responses for urea-N were received but were not specifically requested in the questionnaire.)			
	Urea is colorimetrically determined with diacetyl monoxime and thiosemicarbazide in the presence of sulphuric acid, phosphoric acid, and ferric chloride.	Rahmatullah and Boyde, 1980	NOAA/AOML	Estuarine
		Whitledge, 1981a	SUNY, Stony Brook	
			Brookhaven Nat'l. Laboratory	Estuarine
Soluble Reactive Phosphate	Ortho-phosphate: The determination of reactive soluble phosphate depends on the reaction of phosphate with an acidic molybdate solution. The phosphomolybdic acid which forms is subsequently reduced with ascorbic acid. The resulting molybdenum blue complex is measured at 880 nm.	Murphy and Riley, 1962	U. of Delaware	Estuarine
		Strickland and Parsons, 1972	SUNY, Stony Brook	Estuarine
			U. of Rhode Island	Estuarine
			Old Dominion Univ.	?

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Soluble Reactive Phosphorus (Continued)		Harvey, 1948	NOAA/Great Lakes	Freshwater
		Chamberlain and Shapiro, 1969	NOAA/Great Lakes	Freshwater
		Murphy and Riley, 1962	NOAA/Great Lakes	Freshwater
		Murphy and Riley, 1962, as modified in Whitledge, 1981a	Brookhaven Nat'l. Laboratory	Estuarine
		Technicon AAII, 1973 (Method No. 155-71W)	Case Western Reserve	Freshwater
			NOAA/AOML	Estuarine
			NOAA/Sandy Hook	Estuarine
		Technicon AAII method as modified by Gardner and Malczyk, 1983	NOAA/Great Lakes	Freshwater
		Davis and Simmons, 1979	U. of Michigan	Freshwater
	As above using stannous chloride as the reductant.	Technicon AAII, however, using the stannous chloride technique described by Harvey, 1948	Ohio State U.	Freshwater
		Grasshoff, 1976	U. of Georgia	Estuarine

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Dissolved Organic Phosphorus	(The following responses for dissolved organic phosphorus were received but were not specifically requested in the questionnaire.)			
	UV oxidation	Armstrong et al., 1966	Brookhaven Nat'l. Laboratory	Estuarine
	Wet oxidation with potassium persulfate in an acidic medium	Menzel and Corwin, 1965	Ohio State U.	Freshwater
		Solorzano and Sharp, 1980b	U. of Rhode Island	Estuarine
			U. of Delaware	Estuarine
		Technicon AAII, Method No. 1976 329-74W/A, as modified by Gardner and Malczyk, 1983	NOAA/Great Lakes	Freshwater
Particulate Phosphorus and/or Total Phosphorus	(The following responses for particulate phosphorus and/or total phosphorus were received but were not specifically requested in the questionnaire.)			
	Dry combustion and acid hydrolysis	Solorzano and Sharp, 1980b	U. of Delaware	Estuarine
			U. of Rhode Island	Estuarine
	Block digestion, add 360C with K^2SO_4.	AAII, 1976, Method No. 329-74W/A, as modified by Gardner and Malczyk, 1983	NOAA/Great Lakes	Freshwater
	Persulfate digestion	Standard Methods, 15th ed., 1980	Old Dominion Univ.	?
		Menzel and Corwin, 1965	U. of Michigan	Freshwater

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Dissolved Silica	This automated procedure for the determination of soluble silicates is based on the reduction of a silicomolybdate in acidic solution to "molybdenum blue" by ascorbic acid. Oxalic acid is introduced to the sample stream before the addition of ascorbic acid to eliminate interference from phosphate.	Mullin and Riley, 1955	NOAA/AOML	
		Davis and Simmons, 1979	U. of Michigan	Freshwater
	As above, substituting metol-sulphite for ascorbic acid and reading the blue reduction complex at 810 nm.	Strickland and Parsons, 1972	U. of Delaware	Estuarine
		Strickland and Parsons with cautions described by Pilson et al., 1973	U. of Rhode Island	Estuarine
		Technicon Auto-Analyzer Method 186-72W	Ohio State U.	Freshwater
			Case Western Reserve	Freshwater
			NOAA/Sandy Hook	Estuarine
	As above except for sulphite reduction with disodium EDTA and read at 700 nm.	Rainwater and Thatcher, 1960	NOAA/Great Lakes	Freshwater

TABLE 1 (Continued)

Nutrient	Name and Principle of Method	References	NOAA Users	Matrix
Dissolved Silica (Continued)	As above except that stannous chloride reduction is used and samples are read at 820 nm.	Armstrong et al., 1967, as modified by Whitledge, 1981a	Brookhaven Nat'l. Laboratory	Estuarine
Particulate Silica	Wet alkaline digestion	Krause et al., 1983	NOAA/Great Lakes	Freshwater

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Figure 1. **Evaluation Sheet for NOAA Quality Assurance Program, December 1983**

Investigator(s): _____

Laboratory: _____

	Nutrient*									Notes
	NH_4	NO_3+NO_2	SRP	TDP	TP	DSi	PSi			
Purpose and use of data: Monitoring = M Research = R										
Mode of publication: Refereed journals = J Reports = R Computerized data files = C										
Approximate number of samples per year: Give number										
Method of analysis: AutoAnalyzer = AA Manual = M Other = O										
Method reference provided? Yes = Y No = N										
Method extensively modified? Yes = Y No = N										
Is quality assurance documented?: Yes = Y No = N										

Whole Report Score: _____

Excellent = 3
Good = 2
Fair = 1
Poor = 0

*NH_4 = ammonium; NO_3+NO_2 = nitrate + nitrite; SRP = soluble reactive phosphorous; TDP = total dissolved phosphorous; DSi = dissolved reactive silica; PSi = particulate silica.

	Nutrient										Notes
	NH_4	NO_3+NO_2	SRP	TDP	TP	DSi	PSi				
Precision defined? Yes = 1 No = 0											
Precision evaluated? With standards and samples = 3 Only with standards = 2 Not distinguished = 1 Not evaluated = 0											
Accuracy evaluated with standard reference materials? Yes = 4 No = 2 Not mentioned = 0											
Accuracy evaluated with independent method or by standard addition? Yes = 2 No = 1 Not mentioned = 0											
Are calibration curves (or other quantification methods) run or checked with each sample set? Adequate = 6 Minimally adequate = 3 Inadequate = 0 Not mentioned = 0											
Is handling from sampling to analysis replicated? Adequate = 2 Minimally adequate = 1 No samples = 0 Not mentioned = 0											
Sample collection and storage											
1. **Are contaminant precautions taken?** Adequate = 2 Minimally adequate = 1 Inadequate = 0 Not mentioned = 0											

	Nutrient										Notes
	NH_4	NO_3+NO_2	SRP	TDP	TP	DS1	PS1				
2. Are sample storage problems addressed? Adequate = 2 Minimally adequate = 1 Inadequate = 0 Not mentioned = 0											
Are reagent blanks run with each sample set? Always = 2 Sometimes = 1 Never = 0 Not mentioned = 0											
Are analyses replicated? Some samples = 2 No = 0 Not mentioned = 0											
Are blind standards included in analyses? Yes = 1 No = 0 Not mentioned = 0											
Are interlaboratory comparisons made? Yes = 2 No = 1 Not mentioned = 0											
Total points											Grand Total
Mean total _____ (= Grand Total ÷ number of nutrient categories)											_____
Mean Total + Whole Report Score _____											

Maximum Possible Score = 32

APPENDIX I

FROM THE QUALITY CONTROL HANDBOOK FOR
PILOT WATERSHED STUDIES, PLUARG, IJC

Revised March 13, 1980
J. L. Clark

REPORTING LOW LEVEL DATA

There are specific problems in the reporting of low level data which are associated with the question: is a substance present? While this question is seldom germane in IJC work concerned with loading estimation, it has so influenced thinking about reporting low level data that it seems best to consider it in some depth before dealing with how such data are to be reported for IJC purposes.

In answering the question "is a substance present?", there are two possible correct conclusions which may be reached. One may conclude that the substance is present when it is present, and one may conclude that the substance is not present* when it is not present. Conversely, there are two possible erroneous conclusions which may be reached. One may conclude that the substance is present when it is not, and one may conclude that the substance is not present when it is. The first kind of error, finding something which is not there, is called a TYPE I ERROR. The second kind of error, not finding something which is there. is called a TYPE II ERROR.

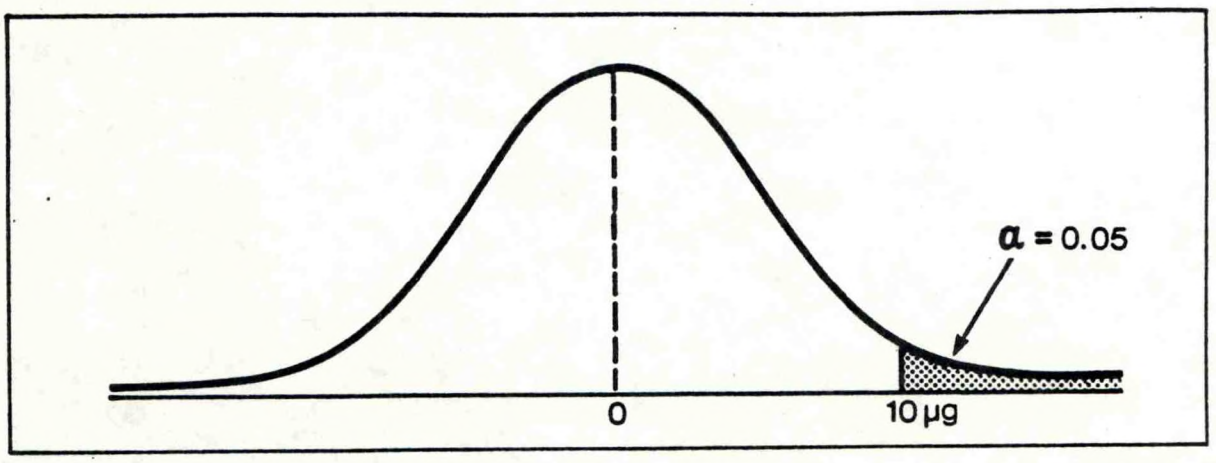
These two types of errors are illustrated in the material that follows, using the result which might be obtained from a single analysis when the substance is not present to illustrate Type I error and the inferences that might be drawn from a single analysis at two different actual concentrations to illustrate Type II error.

Of course inferences as to water quality are seldom, if ever, based on the result of a single analysis. A single result is used here to simplify the exposition.

*Since Avogadro's number is very large, a pedant could argue that one should never claim that a substance is not present. A common sense meaning of not present is intended here, i.e. if measurement is being made in micrograms per litre the presence of a few nanograms per litre is irrelevant.

If the standard deviation, σ, of an analytical procedure has been determined at low concentrations including 0, then the probability of making a Type I error can be set by choosing an appropriate α level to determine the Criterion of Detection.†

For example, suppose that the standard deviation, σ, of an analytical procedure is 6 µg/litre and that an α of 0.05 is deemed acceptable so that the probability of making a Type I error is set at 5%. The Criterion of Detection can then be found from a table of cumulative normal probabilities to be $1.645\ \sigma = 1.645 \times 6$ µg/litre $\simeq$ 10 µg/litre.



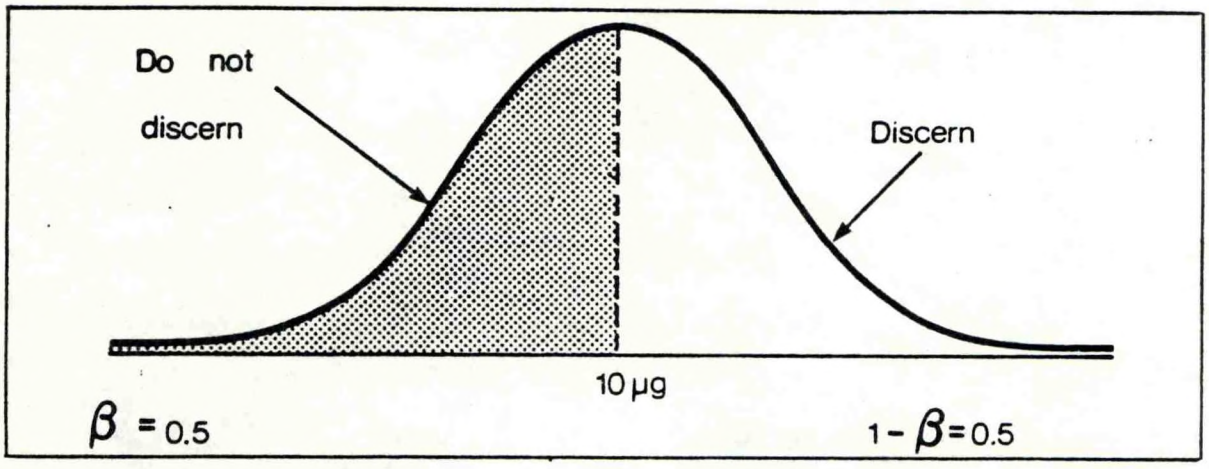
Any value observed below 10 µg/litre would be reported as less than the Criterion of Detection, since to report such a value otherwise would increase the probability of making a Type I error beyond 5%.

Note that the context of decision is the analytical result produced by the laboratory. A result is obtained and a response made to it. Nothing has been said concerning the ability to detect a substance which is present at a specified concentration.

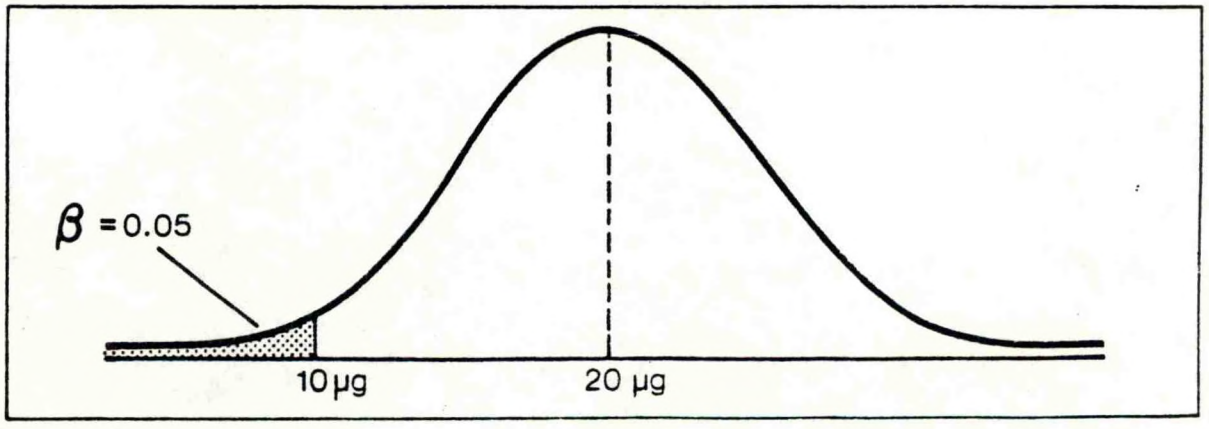
†Criterion of Detection may be a new term to some. It refers to the minimum analytical result which must be observed before it can be stated that a substance has been discerned with an acceptable probability that the statement is true. The terms Detection Limit or Limit of Detection are often used with this meaning, but in this Handbook they are reserved for a more appropriate usage.

Once the Criterion of Detection has been set, the probability of making a Type II error, β, or its complement $1-\beta$, the probability of discerning the substance when it is present, can be determined for given true situations. (The probability $1-\beta$ is sometimes called the power of the test).

Consider the same analytical procedure as above with a Criterion of Detection of 10 µg/litre. Suppose that the concentration of the sample being analyzed is 10 µg/litre, i.e. the concentration is equal to the Criterion of Detection.. If, all analytical results below the Criterion of Detection were reported as such, then the probability of discerning the substance would be 0.5 or 50%.



Conversely, the probability of making a Type II error and failing to discern the substance would also be 0.5. From this example it can be seen that the probability of discerning a substance when its concentration is equal to the Criterion of Detection is hardly overwhelming. In order for the probability of a Type II error to be equal to the probability of a Type I error, $\beta = \alpha$, then the concentration of the sample being analyzed must be twice the Criterion of Detection.



This concentration of twice the Criterion of Detection is the Limit of Detection when it has been decided that the risk of making a Type II error is to be equal to the risk of making a Type I error.

The concept of Type II error has been emphasized because it is usually ignored. Generally, attention is paid to the avoidance of Type I error with no consideration given to the probability of making a Type II error. It should also be recognized that when the probability of making a Type I error is decreased by selecting a lower α-level, the probability of making a Type II error is increased.

Having, it is hoped, made clear the conceptual context in which an α-level is set and the difference between the Criterion of Detection and the Limit of Detection, IJC requirements in the reporting of low level data can be considered.

> *In general, only under highly exceptional circumstances need there be a concern with avoiding Type I error when reporting data for IJC purposes.*

There are two reasons why Type I error is not a concern. First, the IJC is not an enforcement agency, and therefore is not concerned that a single datum will lead it into a false accusation that a substance is present when it is not. Second, in virtually all cases data are aggregated for IJC purposes in order to provide estimates of loadings and/or concentrations; therefore the avoidance of Type I error relates to data sets and not to the individual datum.

This second point is crucial. Rarely, if ever, will the analytical chemist have responsibility for inference from data sets or even be in a position to know which data may be combined. Therefore, censoring of results to prevent a possible faulty inference being drawn from an individual datum represents an unwarrented assumption of responsibility.

In practice, these considerations mean that the Criterion of Detection may be set as low as possible. To state it another way, the α-level may be ignored.

On the other hand, when reporting data for IJC purposes every effort must be made to avoid Type II error.

The reason is obvious. When results are reported as "less than" or "below the Criterion of Detection," they are virtually useless for either estimating loadings or concentrations.

In practice, this consideration means that if a number can be obtained, it is to be reported.

CODES TO BE USED IN REPORTING LOW LEVEL DATA

At its April 12, 1976 meeting the Data Quality Subcommittee of the Water Quality Board passed a resolution that 2 new codes be made available in data storage systems for remarks concerning data used in IJC reports. The codes are T and W.

The T code has the following meaning: "Value reported is less than Criterion of Detection." The use of this code warns the data user that the individual datum with which it is associated does not, in the judgement of the laboratory which did the analysis, differ significantly from 0.

It should be recognized that an implied significance test which fails to reject the null hypothesis that a result does not differ from a standard value in no way diminishes the value of the result as an estimate. To illustrate: a result of 9 µg on a test whose σ = 6 µg can not be regarded as significantly different from 0 for any α-level less than 0.067; however, if a significance test were made with α = 0.1, then the null hypothesis would be rejected and the result deemed significantly different from 0.

So the result, 9 µg, could be reported as "Below the Criterion of Detection" for all α less than 0.067 and could be reported as simply "9 µg" for all α greater than 0.067. But however reported, the result of 9 µg remains the best estimate of the true value since changing the risk of making a Type I error neither augments or diminishes the value of an estimate.

It may be added that low level results are better estimates, in the sense of being more precise, than higher results since for all analytical tests with which we are acquainted the standard deviation of the test increases with the concentration.

The W code has the following meaning: "Value observed is less than lowest value reportable under T code." This code is used when a positive value is not observed or calculated for a result. In these cases the lowest reportable value, which is the lowest positive value which is observable, is reported with the W.

The following example illustrates the use of the codes:

Suppose that a laboratory has determined that its Criterion of Detection for total phosphorus is 10 µg/litre, and suppose in addition that the smallest increment that can be read on the analytical device corresponds to a concentration of 2 µg/litre. Given these conditions, any value observed $\geq$10 µg/litre would be reported without an accompanying code; any value observed $\geq$2 µg and <10 µg would be reported with the T code; if no instrument response were observed, the result would be reported as 2W.

REPORTING NEGATIVE RESULTS

With many analytical procedures there will always be an instrument response, so the W code will not apply. In particular, this lack of applicability will occur when a result is obtained through subtraction of a blank correction. In this case negative results will often be obtained; in fact, if the constituent of interest is not present, one would expect negative results to occur as often as positive.

In order that valid inferences may be made from surveillance data, it is important that negative results be reported as such. Consider the following three different ways of reporting the same results. The left hand column gives results in a heavily censored form; the center column has negative results censored; the right hand column gives the results as obtained.

<3 µg	2 µg	2 µg
<3	0	-2
<3	0	-1
4	4	4
3	3	3
<3	0	-3
<3	1	1
<3	0	-1
<3	0	0
<3	2	2

Nothing can be done with the results in the left hand column except to conclude that we don't know whether the constituent is present or not; the sampling and analytical effort have been wasted.

If the results in the center column were taken at face value, one could conclude that the mean concentration was 1.2 µg with a standard error of the mean of 0.467 and 95% confidence limits for the mean of 0.14 µg and 2.26 µg. Since the confidence limits do not include zero, it would appear that the evidence supports the presence of the constituent.

Analysis of the uncensored results of the right hand column gives a mean concentration of 0.5 µg, a standard error of the mean of 0.719, and 95% confidence limits for the mean of -1.13 µg and 2.13 µg. The correct conclusion can be drawn that the evidence is insufficient to support the presence of the constituent.

Note that the censored data of the center column distort both the mean and the standard error of the data, making the data appear more precise than they are.

Of course any result of 0 or less which is reported should be reported with the T code.

SUMMARY

A technical working group's analysis of 13 quality assurance reports, submitted by NOAA-supported nutrient laboratories, suggests that NOAA is using state-of-the-art methodology to produce high-quality nutrient measurements for marine and Great Lakes samples. Quality control practices of most of these laboratories compare favorably with those used by other investigators in the field. Examples of good quality assurance practices reported were: the use of daily calibration curves and blank determinations, minimization of contamination and sample storage problems, use of standard reference materials when feasible, and adequate sample and analysis replication. Quality assessment (i.e. verification and documentation of quality control) was less adequate than were the quality control measures. Precision was often not adequately defined in the reports. Blind standards or standard addition techniques, to check accuracy and precision, were not used as often as desirable. Several laboratories took part in interlaboratory comparisons but not as often nor for as many nutrients as optimum, in part because some nutrient forms are not stable during prolonged sample storage.

The working group's recommendations for the future are:

To NOAA Management:

1. Recognize the high cost of adequate quality assurance programs.

2. Encourage technical project officers to include a strong quality assurance component in outside NOAA contracts for nutrient analysis.

3. Improve NOAA quality assurance guidelines.

4. Provide information on availability of standard reference materials.

5. Implement preparation of new standard reference materials.

6. Encourage interlaboratory comparisons among groups with similar samples, but do not implement a NOAA-wide intercalibration program.

7. Periodically review analytical and quality-assurance procedures for nutrient analysis in NOAA and NOAA-supported laboratories.

8. Be specific on requested details if future quality assurance questionnaires are used.

9. Periodically distribute nutrient analysis information among scientists within and supported by NOAA.

To NOAA and NOAA-Funded Laboratories:

1. Consider quality assurance guidelines in planning research and monitoring programs.

2. Calibrate laboratory instruments and prepare standards at specified intervals.