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2006 Inter-laboratory Comparison Study for Reference Material for Nutrients in Seawater

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栄養塩測定用海水組成標準の2006年国際共同実験報告

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Preface

The history of the analysis of nutrients in seawater is long. Nutrients and total inorganic carbon have been the major observational variables in various international global ocean observation expeditions, such as the Geochemical Ocean Sections Study and the World Ocean Circulation Experiment (WOCE). Observation of the natural variability of nutrients and inorganic carbon in the world's oceans, and investigation of temporal and spatial changes due to the oceans' response to climate change and increasing carbon dioxide in the atmosphere, continue to be important topics of oceanographic research. To address the need for highly accurate and precise data regarding the effects of climate change on nutrient concentrations, the WOCE Hydrographic Program office proposed criteria for the precision and accuracy of nutrient analysis in early 1990. However, attaining these criteria was not possible, owing to the lack of an accepted standard or reference materials for nutrients in seawater that was applicable to the Pacific Ocean, where the maximum nutrient concentrations are greater than in the Atlantic and Indian Oceans. Current knowledge about the variability of nutrient concentrations in seawater is limited because the variation is very small. Therefore we need traceability and comparability of the nutrients data as well as high accuracy and high precision of them.

The Geochemical Research Department of the Meteorological Research Institute (MRI) of Japan started to develop seawater-based reference materials for nutrient analysis about ten years ago. This research continues today as part of the "Observational Study on the Variability of the Carbon Cycle in the Ocean, I (2004–2006) and II (2007–2008)". A major goal of this research is the development of standard materials for the analysis of nutrients in seawater that satisfy the requirements for oceanographic research. The MRI research comprises three parts: the development of seawater-based reference materials, the conducting of global inter-laboratory comparison study to use and test the reference materials, and the practical use of the reference materials on board the R/V *Mirai* of Japan Agency for Marine-Earth Science and Technology (JAMSTEC) during a series of research voyages. We are now progressing towards having seawater-based nutrient reference materials with stability and homogeneity that are sufficient to satisfy our present requirements. To establish a standard material for nutrient analysis in seawater, an inter-laboratory comparison study in the world is an important step.

This technical report summarizes results of the second inter-calibration exercise conducted by MRI, in which 52 laboratories participated.

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序文

海水中の栄養塩の分析は長い歴史がある。海水栄養塩分析の海洋学的目的の一つは、海水中の栄養塩濃度の自然変動、及びそれに関連して大気中の二酸化炭素の増大やその結果引き起こされる気候変動に応答した海洋の栄養塩の変動を検出することにある。事実、過去にGEOSECSやWOCE等の時代を画するような世界的プロジェクト研究が実施されてきたが、この中で海水中の栄養塩は重要な測定項目として取り上げられてきた。特に、1990年代に実施されたWOCEでは、海洋における栄養塩の変動を検出するため必要とされる分析精度や確度についての目標値が提案された。しかし、最近まで海水中の栄養塩の分析では、提案された基準（特に、確度）を満足することができていない。その主要な原因は、海水中の栄養塩の分析に関して、基準を満足させるための標準物質ないし参照物質が提供されなかったためである。そのため、現在に至るも海洋における栄養塩の変動に関する知識は限られている。従って、変動を検出するためには、高精度であるばかりでなく追跡可能性（トレーサビリティ）や比較可能性（コンパラビリティ）のある栄養塩データを得るために必要な標準物質ないし参照物質の確立が求められている。

1990年代の中頃より、気象研究所地球化学研究部（青山）では、海水をベースにした栄養塩の参照物質を作成する研究を始めた。この数年間は、融合型経常研究「海洋における炭素循環の変動に関する観測的研究I（平成16～18年度）及びⅡ（平成19～20年度）」の一部としてこの研究が進められている。主要な目標は、海水中の栄養塩分析に関して海洋学的要求を満たした標準物質システムを構築することである。この研究は、1：海水ベースの栄養塩参照物質の開発、2：参照物質とするための国際比較実験の実施、3：観測船「みらい」の船上での栄養塩分析における参照物質の実用試験からなる。現在、栄養塩参照物質の開発に関して、この条件を満たし安定でしかも均一な海水ベースの参照物質を作成しつつある。この標準物質システム構築の過程で、必要な一歩として、この国際的な相互比較実験がある。

この技術報告では、52機関の参加で得られた第2回国際相互比較実験の結果が取りまとめられている。

地球化学研究部長　　廣瀬勝己

Abstract

Autoclaved natural seawater collected in the North Pacific Ocean was used as a reference material for analysing nutrient concentrations in seawater during an inter-laboratory comparison study conducted in 2006; this study was a follow-up to a similar but smaller study conducted in 2003. Homogeneity of sample #2 was confirmed by the repeatability of the nutrient concentration measurements and those interms of one sigma of standand deviation are: 0.2%, 0.3%, and 0.2% for nitrate, phosphate and silicate, respectively. Sets of six samples with concentration ranges of 0.1–42.4 μmol kg^{-1} for nitrate, 0.0–0.6 μmol kg^{-1} for nitrite, 0.0–3.0 μmol kg^{-1} for phosphate, and 1.7–156.1 μmol kg^{-1} for silicate were analysed. A set of samples was distributed to each of 55 laboratories around the globe (20 countries), and results were returned by 52 of those laboratories (19 countries).

Analytical precisions reported by the participating laboratories for all deteminands were generally lower, by at least 50%, than the consensus standard deviations of the reported concentrations. The consensus standard deviations for sample #2 for all determinands were 5 to 10 times as large as the homogeneities of sample #2 for all determinands. In some laboratories, the non-linearity of the calibration curve was not treated effectively.

Our results indicate that variability in the in-house standards of the participating laboratories and the handling of the non-linearity of the calibration curve of the participating laboratories were the primary sources of inter-laboratory discrepancies. The results confirm that a certified reference material for nutrients in seawater and a common method for measuring nutrient concentrations are essential for the improvement of the global comparability of nutrient data in the world’s oceans.

要旨

栄養塩測定用海水組成標準の2006年国際共同実験が行われた、この国際共同実験では、オートクレーブで滅菌処理された天然海水が試料として用いられた。これらの試料は、栄養塩測定用海水組成標準の2003年国際共同実験で用いられたものと同様に処理されたものである。試料の均一性は、硝酸塩において0.2%、リン酸塩において0.3%、ケイ酸塩において0.2%であった。六本一組で用いられた試料の濃度範囲は、硝酸塩が0.1 – 42.4 μmol kg^{-1}，亜硝酸塩が0.0 – 0.6 μmol kg^{-1}，リン酸塩が0.0 – 3.0 μmol kg^{-1}，ケイ酸塩で1.7 – 156.1 μmol kg^{-1} である。20カ国55機関に試料が送付され、19カ国52機関から結果が報告された。

各機関から報告された全分析項目の分析繰り返し精度は、報告された値のコンセンサス（合意）濃度の標準偏差（1シグマ）の半分あるいはそれ以下という値であった。試料番号2について、報告された濃度から導かれたコンセンサス（合意）濃度の標準偏差（1シグマ）は、全分析項目において試料の均一性の5倍から10倍の大きさであった。また、いくつかの機関において分析時に検量線の非直線性を十分に考慮していないことが見出された。

これらの結果は、各機関における栄養塩分析用標準液の違いと分析時における検量線の非直線性の扱い方の違いが、各機関相互の栄養塩濃度の報告値の違いの主たる原因であることを示している。従って、認証標準物質の使用と栄養塩分析における手法の共通化が、全海洋での栄養塩データの追跡可能性（トレーサビリティ）と比較可能性（コンパラビリティ）を確立するために重要である。

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1. Introduction

The objective of this inter-laboratory comparison study was to continue our work on the development of a reference material for analysis of nutrients in seawater that would ensure the comparability of nutrients data measured by different laboratories and that would facilitate shipboard analysis of nutrients in seawater. In particular, we are focusing on developing a reference material with a seawater matrix. The development of such a reference material would make highly accurate nutrient data from different laboratories more widely available. The IOC–IAEA–UNEP (Intergovernmental Oceanographic Commission – International Atomic Energy Agency – United Nations Environment Programme) Group of Experts on Standards and Reference Materials (United Nations Educational, Scientific and Cultural Organization (UNESCO), 1991, 1992) had already clearly stated the need to place a high priority on developing such a reference material.

Currently, the only way to ensure comparability among nutrient analyses performed by different laboratories was to conduct inter-laboratory comparison studies that provide consensus values plus uncertainties for nutrient concentrations. Five ICES nutrient inter-laboratory comparison studies have been carried out since 1965 (UNESCO, 1965, 1967; ICES, 1967, 1977; Kirkwood et al., 1991; Aminot and Kirkwood, 1995). In addition to the ICES exercise, other efforts to ensure data comparability have been carried out over the past 30 years or so. For example, in 2000 and 2002, the National Oceanic and Atmospheric Administration (USA) and the National Research Council Canada jointly conducted inter-comparisons between laboratories in the United States and Canada to certify a proposed reference material for nutrients known as MOOS-1, which has a seawater matrix and was developed by the National Research Council Canada (Willie and Clancy, 2000; Clancy and Willie, 2003).

MOOS-1 became first certified reference material for nutrients in seawater (Clancy and Willie, 2004). In addition, a set of certified reference materials, QC-SW3.1, 3.2, 4.1, and 4.2, was developed by Eurofins (2004). However, the nutrient concentrations of MOOS-1 and QC-SW3.1, 3.2, 4.1, and 4.2 are too low for rather than nutrients concertration in Pacific Ocean seawater and could only cover the range of nutrient concentrations in the Atlantic Ocean seawater.

In 2003, the Meteorological Research Institute (MRI) conducted an inter-laboratory comparison study of a newly produced reference material for nutrients in seawater (RMNS). The RMNS samples were prepared with a natural seawater matrix, and the nutrient concentrations were set so as to cover the concentration range of nutrients in the Pacific Ocean, which has the highest nutrient concentrations among the open oceans of the world. Six RMNS samples at different levels of nutrients concertration were distributed to the participating laboratories. The four determinands (nitrate, nitrite, phosphate, and silicate) could be simultaneously analyzed in a single bottole of each RMNS. The standard deviations of the consensus values for phosphate and silicate were 4.5 times and >10 times the corresponding homogeneities. In contrast, the standard deviation of the consensus values for nitrate was only about 2 times the homogeneity. These results indicated that the variability of the in-house standards used by the participating laboratories, rather than analytical precision, was the primary source of inter-laboratory discrepancies. These results confirmed that the use of a certified reference material for nutrients in seawater is essential for establishing nutrient data sets that can be compared between laboratories, particularly for silicate and phosphate.

In 2006, the MRI conducted a second inter-laboratory comparison study that used a strategy similar to that used in the 2003 study. The primary aim of the 2006 study, which was coordinated by Michio Aoyama, was to increase the number of participants relative to the number from the previous study to make the new study as global as possible. This report describes the 2006 study in detail and summarizes the results reported by the participants.

2. Samples

2.1 Preparation of RMNS samples and timetable for the inter-laboratory comparison study

Natural seawater was collected in the North Pacific Ocean at different depths ranging from surface to 1400 m depth, placed in a stainless steel container (100–200 L), and autoclaved twice at 120 ºC for 2 h. Aliquots (90 mL) of the autoclaved seawater were then bottled in polypropylene bottles. This procedure for preparing the RMNS samples was based on a previously reported method for preparing a reference material for the determination of nutrients in seawater (Aminot and Kerouel, 1991, 1995). Long-term storage of the RMNS samples at room temperature has shown that the sample homogeneities and the concentrations of nutrients are maintained for at least 4 years (Aoyama et al., 2006).

Six batches of samples were prepared in 2005. The nutrients concentrations ranged from 0.1–42.4 µmol kg^{-1} for nitrate, 0.0–0.6 µmol kg^{-1} for nitrite, 0.0–3.0 µmol kg^{-1} for phosphate, and 1.7–156.1 µmol kg^{-1} for silicate, respectively. Before sending the samples to the participating laboratories, we confirmed that the nutrient concentrations in the samples were stable for at least several months. By January 2007, 52 participants had analyzed the samples and returned their results.

2.2 Selection of determinands

The determinands of interest were nitrate (or nitrate+nitrite), nitrite, phosphate and silicate.

2.3 Sample homogeneity

Before sending the samples to the participants, we measured the homogeneities of the samples separately. The homogeneities for 30 bottles of sample #2 are listed in Table 1. Analytical precisions (expressed as standard deviation) were also simultaneously estimated for 30 samples of unprocessed natural seawater with nutrient concentrations similar to those of sample #2.

Table 1 Homogeneity of sample #2 and analytical precision

	Nitrate+nitrite %	Phosphate %	Silicate %	Nitrite* %
Homogeneity of sample #2	0.22	0.32	0.19	0.43*
Analytical precision	0.22	0.22	0.12	0.22*
Homogeneity of sample #3 from the 2003 inter-comparison exercise	0.44	0.8	0.15	

Note: The concentrations of nutrients in the unprocessed natural seawater were 43 µmol kg^{-1} for nitrate+nitrite, 3.1 µmol kg^{-1} for phosphate, and 148 µmol kg^{-1} for silicate. *For nitrite, the homogeneity listed is for sample # 1 (nitrite concentration, 0.63 µmol kg^{-1}) and was evaluated based on 229 runs onboard the R/V *Mirai* MR0505 together with analytical precision for a working standard that was prepared from natural seawater (nominal nitrite concentration, 1.2 µmol kg^{-1}).

For sample #2, the homogeneities for nitrate+nitrite, phosphate, and silicate were 0.22%, 0.32%, and 0.19%, respectively. Because the concentrations of nutrients in sample #2 were similar to those in the natural unprocessed seawater used to evaluate analytical precision, the homogeneities for nitrate+nitrite and silicate were of the same order of magnitude as, or better than, the analytical precisions. The homogeneity for phosphate (0.32%) was a little greater than the analytical precision, which was attributed to the nature of the RMNS sample itself rather than to any analytical problem. The homogeneities of the RMNS samples used in this study were generally better than the homogeneities of the RMNS samples used in the 2003 inter-laboratory comparison study (Aoyama, 2006; Aoyama et al., 2007). This improvement was achieved by the electric polish of the surface inside the stainless steel container used to produce the samples.

Samples 1, 3, 4, 5, and 6 were not analyzed as extensively as sample #2, owing to the limited number of available samples. However, it is safe to assume that these samples were similar to sample #2, because all of the samples were prepared by the same process.

3. Participants and response

By August 2006, 55 laboratories (Tables A1 and A2) in 20 countries had replied to the call for participants. A total of 55 sets of samples were then distributed.Table AI in appendix I lists the participants, and cross references the table of laboratories # in 2003 I/C and 2006 I/C, which is shown in table A2. Of the 55 laboratories, 52 submitted results, which are summarized in Table 2.

Results were submitted from 52 laboratories.
The responses from the participants are summarized in table 2.

Table 2 Summary of responses from participants

Nutrient	Sample ID	Number of results	
		Received	Statistically treated
Nitrate+nitrite	1	45	45
	2	44	44
	3	44	44
	4	45	45
	5	41	39
	6	45	45
Nitrate	1	43	43
	2	42	42
	3	42	42
	4	43	43
	5	38	37
	6	43	43
Nitrite	1	47	47
	2	47	47
	3	41	39
	4	47	47
	5	41	39
	6	47	47
Phosphate	1	52	52
	2	52	52
	3	52	52
	4	52	52
	5	48	48
	6	52	52
Silicate	1	46	46
	2	46	46
	3	46	46
	4	46	46
	5	45	45
	6	46	46

4. Statistical treatment

4.1 Raw means, medians, and standard deviations

Raw means, medians, and standard deviations were calculated for the submitted results (Table 3).

4.2 Robust statistics

Robust means (H15 means) and standard deviations (H15 Sd) both ontained by Huber's methos were calculated (AMC, 2001) (Table 3).

4.3 Consensus means, medians, and standard deviations

We applied successive *t*-tests at the 95% confidence level to the results before estimating the consensus means, consensus medians, and consensus standard deviations (Table 4), as in previous inter-laboratory comparison studies (Aminot and Kirkwood, 1995; Aoyama, 2006). Tests were applied until a stable mean was reached; 7 to 10 tests were required for the sets of results.

4.4 Calculation of *Z*-scores

Z-scores were used to evaluate the performance of each participating laboratory, as in previous inter-laboratory comparison studies (Aminot and Kirkwood, 1995; Aoyama, 2006). The *Z*-score for each analysis, Z_{par}, is defined as

$$Z_{par} = \mathrm{ABS}((C_{par} - C_{consensus})/P_{par})$$

where C_{par} is the concentration measured by a laboratory for the parameter of interest (nitrate, phosphate, or silicate); $C_{consensus}$ is the consensus mean sample concentration for the parameter of interest (described in Section 4.3; and P_{par} is the standard deviation of the sample concentration for the parameter of interest. The *Z*-scores for all determinands were calculated. *Z*-scores of each sample for each laboratory were calculated for Z_{NOx} + Z_p and Z_{NOx} + Z_p + Z_s. When nitrate+nitrite was not reported by a laboratory, we used nitrate instead.

5. Results

Results reported by the participants are summarized in Table A3. Raw means, medians, and standard deviations calculated using reported values are summarized in Table 3, together with the robust statistics and the results of successive *t*-tests at the 95% confidence level.

The raw medians of all reported values for the six samples for all determinands were in good agreement with the corresponding consensus means and medians. The robust means for the six samples for all determinands were also in good agreement with the corresponding consensus means and medians.

Scatter plots and histograms for each parameter for each sample are shown in Figures A1-1 to A5- 6; the corresponding consensus value is shown at the top of each figure. In the scatter plots, error bars appear if errors were reported. The histogram interval for each figure was set to equal the corresponding the consensus standard deviation shown in Table 4.

5.1 Ranked scatter plots of the results

Ranked scatter plots for nitrate+nitrite, nitrate, nitrite, phosphate, and silicate are shown in Figures 1–5, respectively. For nitrate and phosphate, laboratories were ranked according to the reported concentrations of nitrate and phosphate in sample #3, which had the highest nitrate and phosphate concentrations of all the samples. For silicate, laboratories were ranked according to the reported silicate concentration in sample #2, which had the highest silicate concentration of all the samples. For nitrate, laboratories were ranked according to the reported nitrate concentration in sample # 1, which had the highest silicate concentration of all the samples.In Figures 1 to 5, error bars appear if errors were reported.

If each laboratory adequately handled the non-linearity of the calibration curves, we would expect the ranked concentration plots to be proportional to each other for the samples of differing concentrations. However, there were non-proportional results from some laboratories for all the determinands (Figures 1 to 5). Several laboratories reported that they used a straight line for the calibration. We observed non-proportional results in Figures 1 to 5 in cases in which the calibration curve was in fact non-linear (curved), because the analytical systems used were not analytically optimized as they should have been for those nutrient values.

These results indicate that non-linearity of the calibration curves for nutrient analysis was a significant source of error, in addition to the non-linear value-dependent errors.

Table 3 mean, median and standard deviation of reported values, results of robust statistics, and consensus mean and consensus median

nutrient	sample #	n	raw mean µmol Kg-1	raw median µmol Kg-1	raw SD µmol Kg-1	H15 mean µmol Kg-1	H15 SD µmol Kg-1	consensus mean µmol Kg-1	consensus median µmol Kg-1
Nitrate+Nitrite	1	45	6.17	6.28	0.51	6.22	0.33	6.32	6.29
	2	44	33.12	33.61	2.20	33.53	0.90	33.69	33.69
	3	44	41.41	42.29	3.83	42.27	1.20	42.47	42.42
	4&6	91	21.37	21.88	2.45	21.84	0.87	22.00	21.98
	5	39	0.17	0.05	0.34	0.01	0.01	0.02	0.01
Nitrate	1	43	5.60	5.64	0.48	5.63	0.30	5.68	5.67
	2	42	33.15	33.56	2.18	33.54	0.82	33.58	33.58
	3	42	41.49	42.25	3.83	42.31	1.03	42.40	42.31
	4&6	87	21.10	21.55	2.39	21.50	0.71	21.60	21.58
	5	37	0.15	0.04	0.34	0.04	0.04	0.04	0.03
Nitrite	1	47	0.63	0.63	0.04	0.63	0.03	0.63	0.63
	2	47	0.11	0.10	0.03	0.10	0.02	0.10	0.10
	3	39	0.04	0.02	0.08	0.02	0.02	0.01	0.01
	4&6	95	0.35	0.35	0.04	0.35	0.03	0.35	0.35
	5	39	0.02	0.02	0.03	0.02	0.02	0.01	0.01
Phosphate	1	52	0.51	0.49	0.11	0.49	0.05	0.49	0.48
	2	52	2.56	2.54	0.43	2.54	0.11	2.52	2.52
	3	52	3.08	3.04	0.25	3.04	0.11	3.03	3.03
	4&6	105	1.60	1.60	0.16	1.60	0.09	1.59	1.59
	5	47	0.06	0.04	0.06	0.04	0.04	0.03	0.03
Silicate	1	46	29.83	30.00	4.04	29.89	1.72	30.15	30.09
	2	46	156.87	155.84	10.26	155.99	4.96	155.74	155.76
	3	46	137.30	135.90	10.61	136.12	3.62	135.36	135.00
	4&6	93	60.67	59.25	12.71	59.42	2.06	58.86	58.77
	5	44	1.80	1.68	0.58	1.72	0.36	1.64	1.64

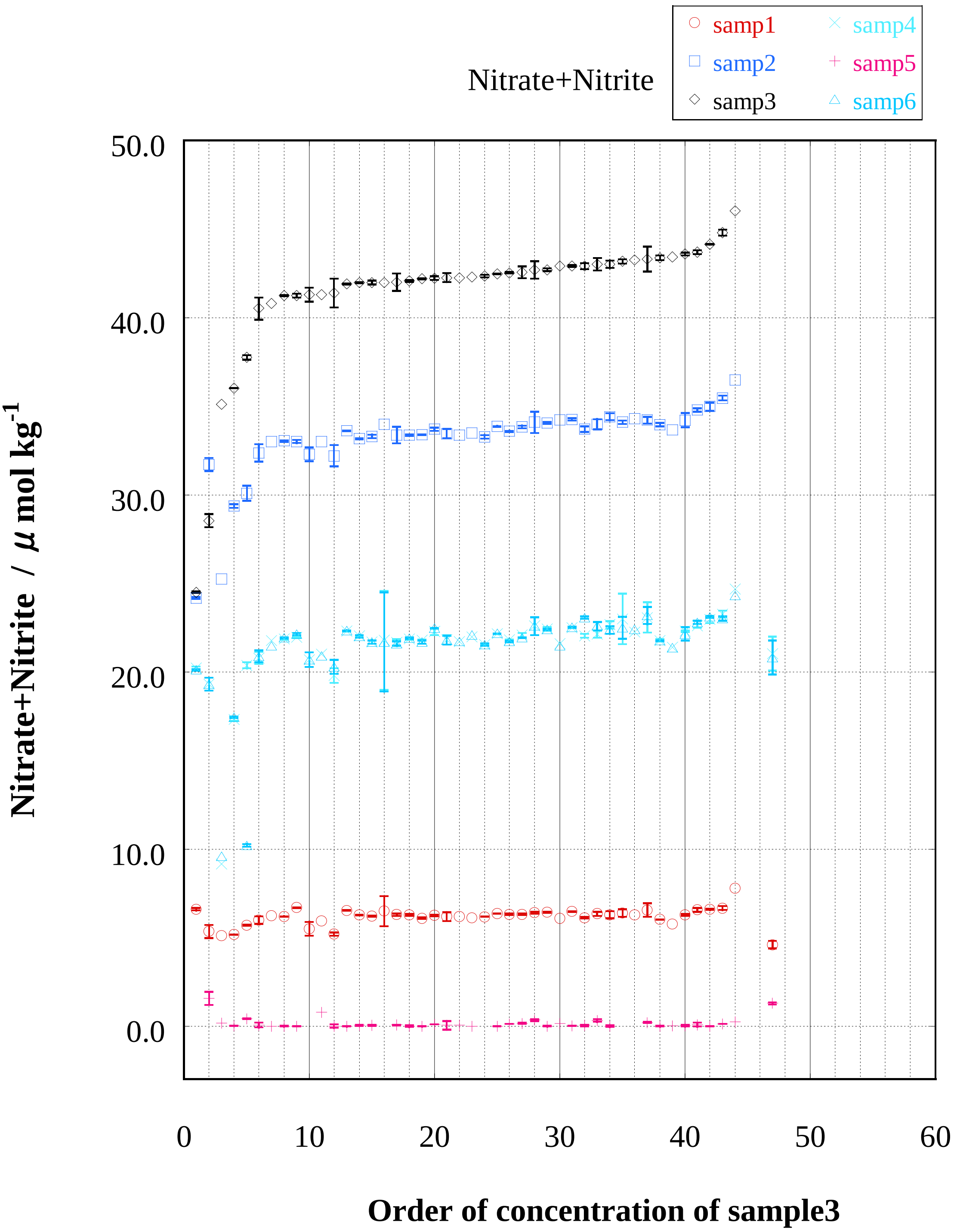

Figure 1 Ranked nitrate+nitrite results for all samples: Reported concentrations were sorted using concentration of sample3.

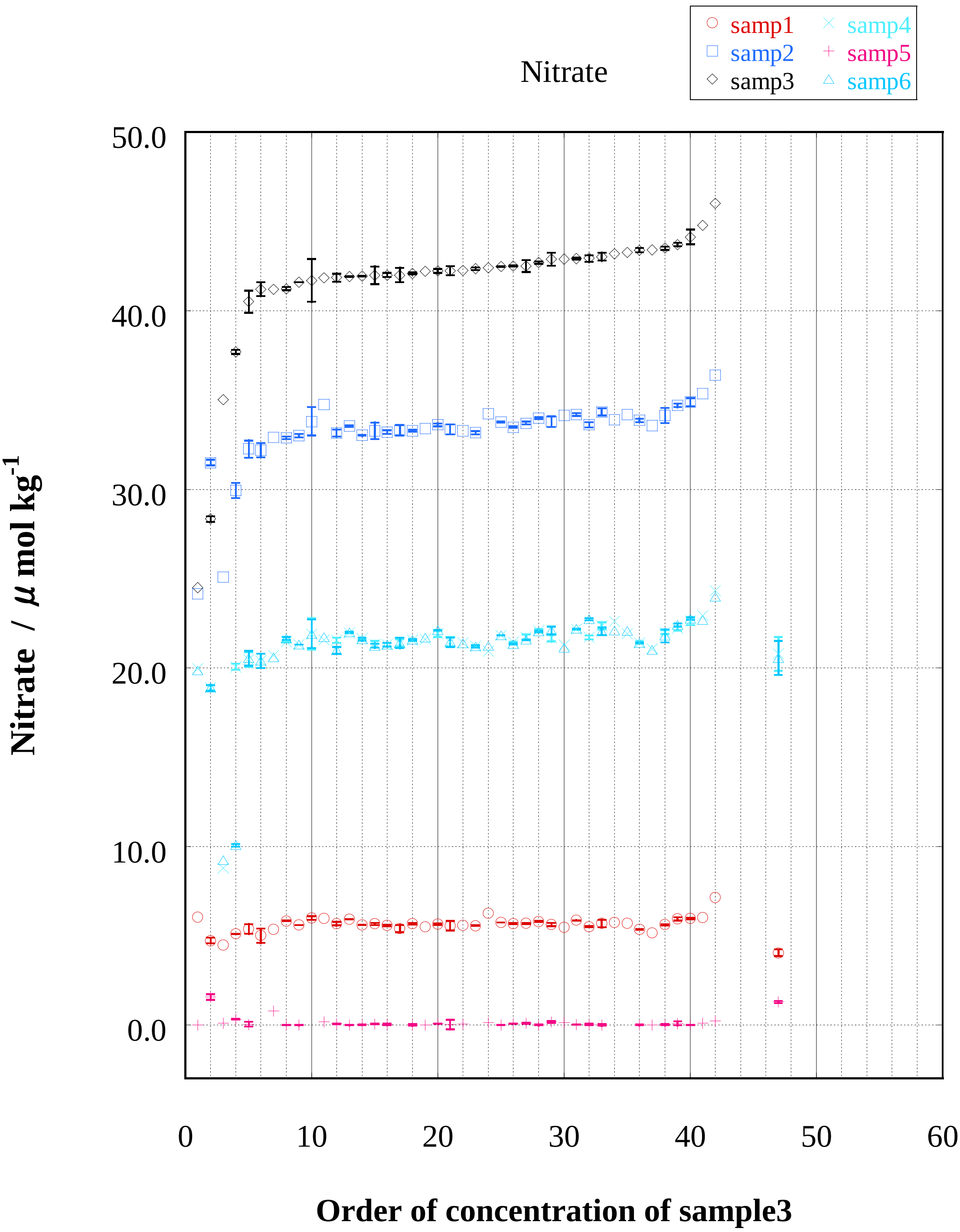

Figure 2 Ranked nitrate results for all samples: Reported concentrations were sorted using concentration of sample3

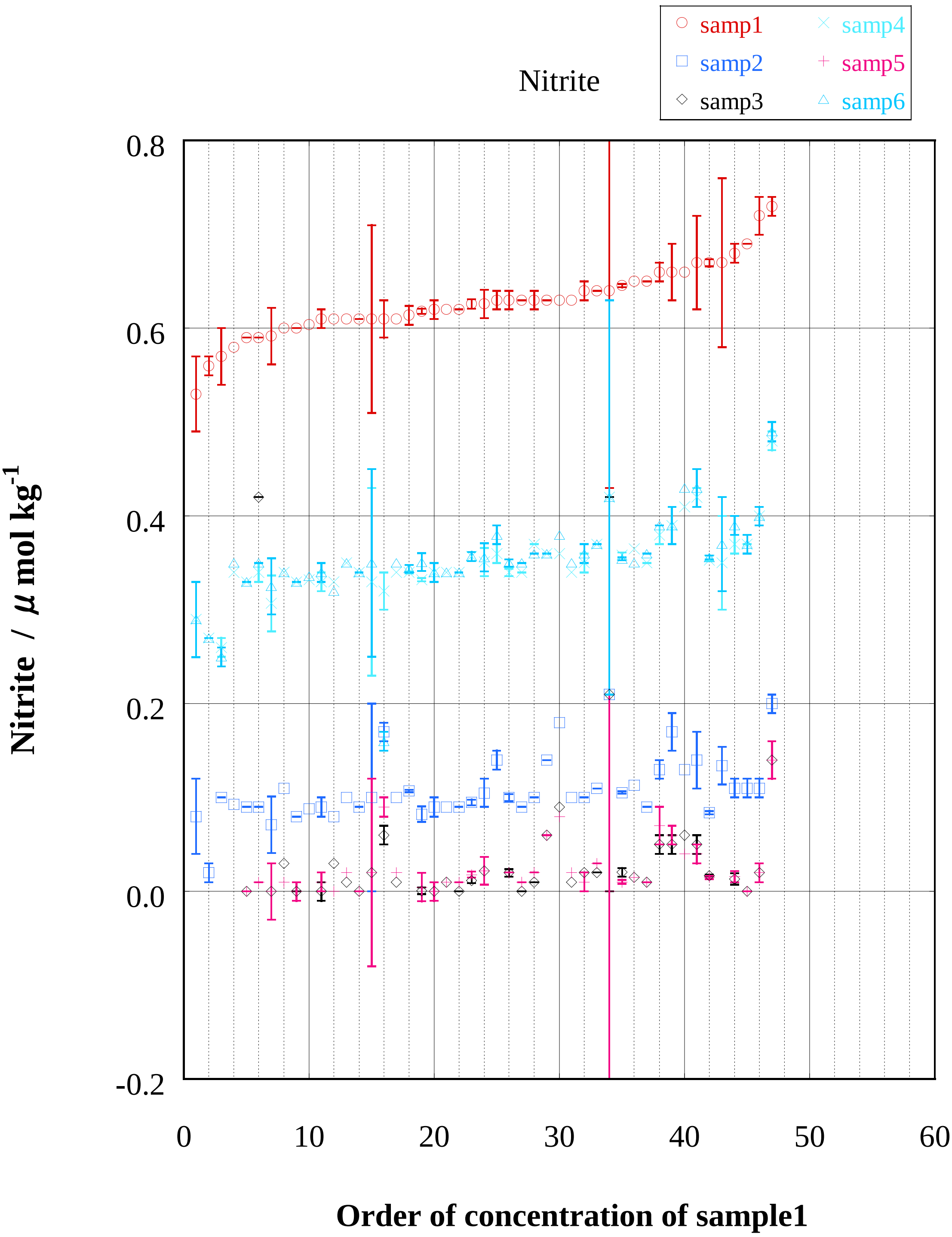

Figure 3 Ranked nitrite results for all samples: Reported concentrations were sorted using concentration of sample1

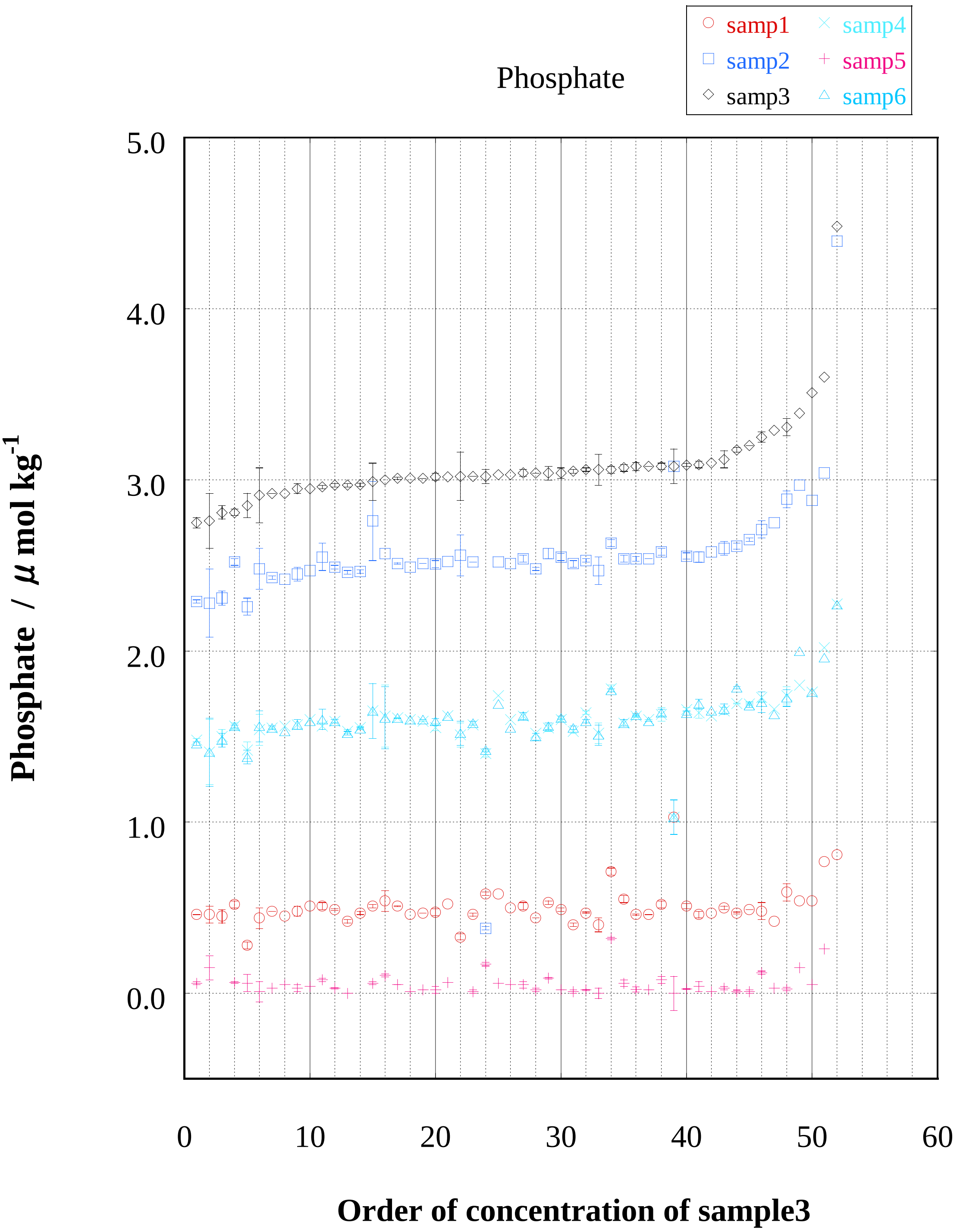

Figure 4 Ranked phosphate results for all samples: Reported concentrations were sorted using concentration of sample3

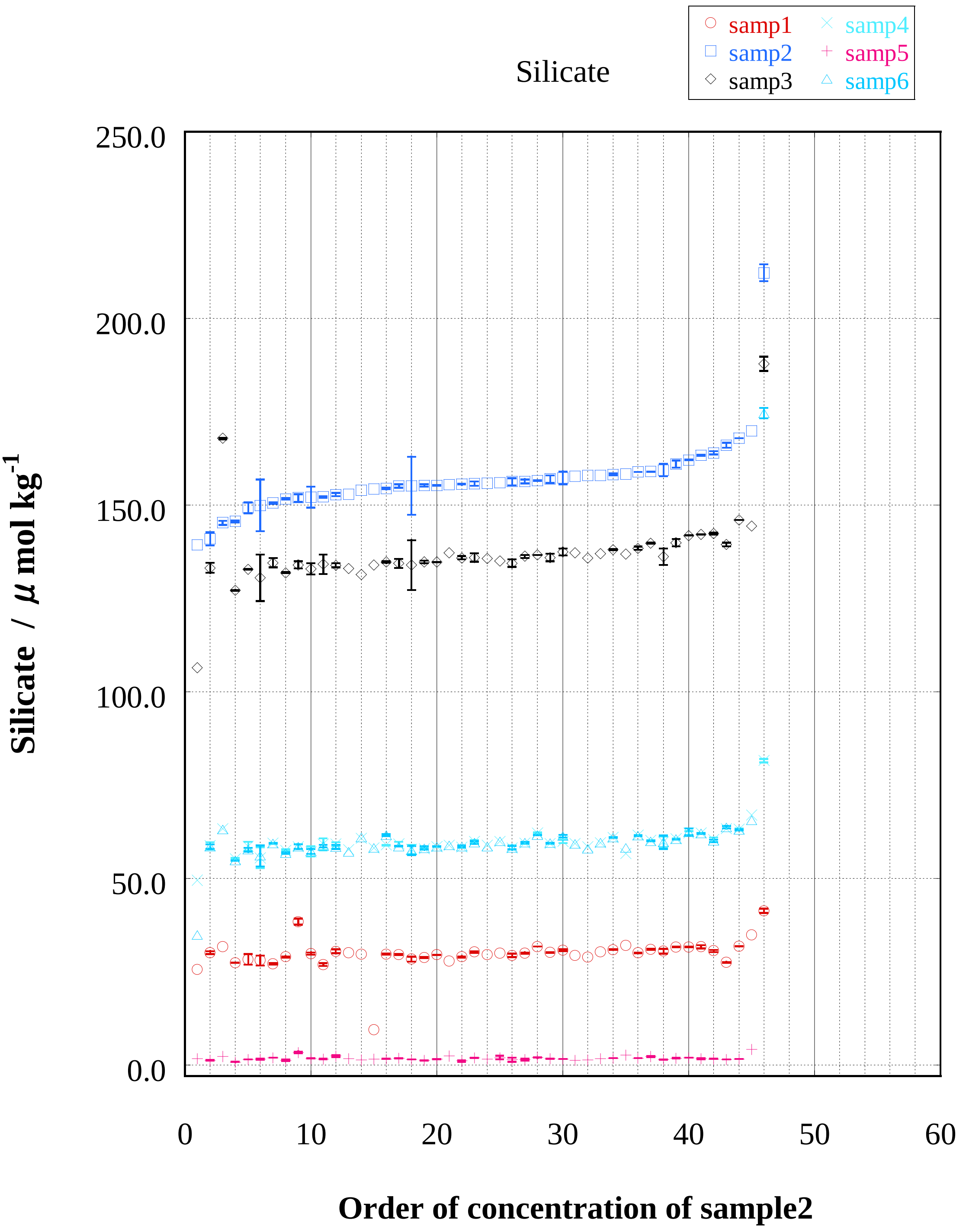

Figure 5 Ranked silicate results for all samples: Reported concentrations were sorted using concentration of sample2

5.2 Consensus medians, means, and standard deviations

We calculated the consensus medians, means, and standard deviations (Table 4) using the data that passed the successive *t*-test applications described in Section 4.3. The consensus means and medians were in excellent agreement for all parameters for all samples.

Table 4 Consensus medians, means, and standard deviations for the 6 samples

nutrient	sample #	n	Consensus Median μmol kg^{-1}	Consensus Mean μmol kg^{-1}	Consensus standard deviation μmol kg^{-1}
Nitrate+Nitrite	1	36(45)	6.29	6.32	0.19
	2	32(44)	33.69	33.69	0.43
	3	34(44)	42.42	42.47	0.70
	4&6	60(90)	21.98	22.00	0.34
	5	24(39)	0.01	0.02	0.02
Nitrate	1	35(43)	5.67	5.68	0.20
	2	31(42)	33.58	33.58	0.42
	3	34(42)	42.31	42.40	0.67
	4&6	61(86)	21.58	21.60	0.33
	5	29(37)	0.03	0.04	0.04
Nitrite	1	40(47)	0.63	0.63	0.02
	2	34(47)	0.10	0.10	0.01
	3	29(39)	0.01	0.01	0.01
	4&6	67(94)	0.35	0.35	0.01
	5	30(39)	0.01	0.01	0.01
Phosphate	1	41(52)	0.48	0.49	0.03
	2	32(52)	2.52	2.52	0.04
	3	35(52)	3.03	3.03	0.04
	4&6	72(104)	1.59	1.59	0.04
	5	38(48)	0.03	0.03	0.02
Silicate	1	36(46)	30.15	30.09	1.06
	2	31(46)	155.76	155.74	2.21
	3	31(46)	135.00	135.36	1.57
	4&6	60(92)	58.77	58.86	0.84
	5	36(45)	1.64	1.64	0.22

Note: *n* represents the number of data points used to calculate consensus means and standard deviations after the successive application of a *t*-test at the 95% confidence level. The numbers in the parentheses represent the numbers of results reported by the participant.

5.3 Comparison between consensus standard deviations and homogeneities for sample #2

For sample #2, the consensus standard deviation for nitrate was 6 times the homogeneity for nitrate (Table 5). For phosphate, the consensus standard deviation was 5 times the homogeneity, and for silicate, the consensus standard deviation was more than 10 times the homogeneity. These results indicate that the use of a common reference material for nutrients in seawater would establish the global comparability of nutrient data for the world's oceans.

Table 5 Comparison between consensus standard deviations of sample #2 and homogeneities of sample #2

	Nitrate %	Phosphate %	Silicate %
Homogeneity	0.22	0.32	0.19
Consensus standard deviation	1.3	1.6	2.0

5.4 Analytical precisions and consensus standard deviations reported by the participating laboratories

Analytical precisions reported by the participating laboratories for the four determinands were generally better than the consensus standard deviations for the reported concentrations. The medians for analytical precision reported by the participants for the four determinands were half or less than the consensus standard deviations (Tables 6-1 to 6-6). Only a few laboratories reported analytical precisions that were larger than the consensus standard deviations.

These results indicate that the analytical precisions for each laboratory might not have caused the larger raw standard deviations and relatively large consensus standard deviations.

Table 6-1.Median and range of analytical precision of participating laboratories and consensus standard deviation for sample #1

Nutrients	Analytical precision of participating laboratory		Consensus standard deviation	
	N	Median(range) %	n	σ %
Nitrate+nitrite	35	0.8(0.1-13.1)	46	3.0
Phosphate	34	3.7(0.4-13.6)	52	6.1
Silicate	32	0.7(0.1-5.0)	46	3.5

Table 6-2.Median and range of analytical precision of participating laboratories and consensus standard deviation (s.d.) for sample #2

Nutrients	Analytical precision of participating laboratory		Consensus standard deviation	
	N	Median(range) %	n	σ %
Nitrate+nitrite	34	0.3(0.1-1.9)	45	1.3
Phosphate	36	0.8(0.2-8.8)	52	1.6
Silicate	30	0.3(0.1-5.0)	44	1.4

Table 6-3.Median and range of analytical precision of participating laboratories and consensus standard deviation for sample #3

Nutrients	Analytical precision of participating laboratory		Consensus standard deviation	
	N	Median(range) %	n	σ %
Nitrate+nitrite	32	0.3(0.1-1.9)	45	1.7
Phosphate	33	0.8(0.1-5.8)	52	1.3
Silicate	30	0.5(0.1-5.0)	44	1.2

Table 6-4.Median and range of analytical precision of participating laboratories and consensus standard deviation for sample #4

Nutrients	Analytical precision of participating laboratory		Consensus standard deviation	
	N	Median(range) %	n	σ %
Nitrate+nitrite	34	0.7(0.1-12.8)	46	1.7
Phosphate	35	1.3(0.1-13.5)	52	2.5
Silicate	31	0.6(0.1-5.0)	45	1.5

Table 6-5.Median and range of analytical precision of participating laboratories and consensus standard deviation for sample #5

Nutrients	Analytical precision of participating laboratory		Consensus standard deviation	
	N	Median(range) %	n	σ %
Nitrate+nitrite	21	40(1.2-500.0)	39	1.3
Phosphate	29	33.3(3.1-600.0)	48	1.6
Silicate	30	4.0(0.4-34.0)	44	1.4

Table 6-6.Median and range of analytical precision of participating laboratories and consensus standard deviation for sample #6

Nutrients	Analytical precision of participating laboratory		Consensus standard deviation	
	N	Median(range) %	n	σ %
Nitrate+nitrite	35	0.5(0.1-12.9)	46	1.7
Phosphate	37	1.3(0.3-14.2)	52	2.5
Silicate	31	0.5(0.1-5.0)	44	1.5

5.5 *Z*-scores

Z-scores, computed according to the method described in Section 4.4, are summarized in Tables 7-1 to 7-7.

Table 7-1 Z-score for nitrate+nitrite

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.3	0.9	1.0	2.9		1.5
2	0.7	1.5	1.7	0.4	0.5	0.2
3	0.2	0.7	0.6	0.4	0.5	0.2
4	1.5	3.0	2.4	2.9	0.9	3.2
5	0.8	1.0	0.1	1.4		1.3
6	5.8	3.5	1.5	6.4	0.9	5.0
7	0.6	0.9	0.7	0.9	1.8	0.9
9	7.6	6.5	5.1	7.8	10.1	6.8
10						
11	0.6	0.9	0.3	1.3	0.5	1.2
12	4.2	3.2	1.7	3.8		3.8
13	0.3	0.4	0.0	0.5	0.9	0.5
14	5.9	10.0	9.2	13.7	0.0	13.3
15	0.0	0.7	0.7	1.0	2.3	1.2
16	0.6	3.9	3.7	3.3	1.1	3.1
17	1.8	4.1	3.3	3.7	4.5	3.0
18	1.0	0.4	0.2	0.0	0.9	0.3
19	1.3	2.6	1.8	1.7	3.2	2.3
20	1.5	22.1	25.6	5.2		5.5
23						
24	2.0	1.6	1.7	0.1	0.9	0.4
25	0.7	0.5	0.3	0.6	1.3	0.6
26	0.0	0.2	0.1	0.5	4.6	0.9
27	0.5	0.9	0.3	1.7	15.6	1.7
28	8.9			2.8	58.7	3.5
29	1.2	0.2	0.8	0.9	0.9	1.0
30	0.2	0.0	0.3	0.8	4.1	1.4
31	2.0	1.6	1.7	2.9	35.7	3.2
32	5.0	4.6	19.8	7.8	71.1	7.8
33	0.0	0.3	0.1	0.3	6.4	0.2
34	0.1	1.2	0.7	0.1	1.3	0.0
35	1.3	1.2	1.2	3.1	8.7	3.5
36						
37	1.5	0.6	1.3	0.7	0.5	0.7
38	0.6	0.7	0.3	0.8	1.3	0.8
39	6.3	19.5	10.5	37.6	7.3	36.2
40						

42	0.1	1.2	1.6	0.9	0.6	0.4
43	0.2	1.7	0.8	1.9	0.9	1.1
44						
45	0.9	0.7	0.7	0.6		0.9
46	1.7	3.1	2.8	3.5	1.8	3.3
47	0.1	1.4	1.2	0.7		1.2
48	1.1	0.7	0.4	0.6	0.9	0.9
49	4.0	1.1	1.0	1.8	13.7	1.7
50	3.2	8.3	6.7	4.7	18.3	34.4
51						
52						
53	1.2	1.3	0.6	1.2	5.9	1.5
54	2.8	0.0	1.4	1.8	0.4	1.9
55	0.8	1.3	0.6	1.5	0.4	1.5
56	0.3	1.6	2.4	0.7	0.5	1.5

Table 7-2 Z-score for nitrate

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.3	0.7	1.2	3.0		1.5
2						
3	0.1	0.7	0.5	0.1	0.9	0.1
4	1.5	3.1	2.6	3.1	0.9	3.5
5	0.7	1.0	0.1	1.2		1.2
6						
7	0.5	0.9	0.6	0.9	0.1	0.9
9	7.5	6.6	5.4	8.2	4.8	7.1
10	1.5	0.7	0.6	0.6	0.9	0.6
11	0.5	0.9	0.4	1.5	0.9	1.4
12	3.5	3.3	1.8	3.6		3.6
13	0.3	0.4	0.1	0.7	0.9	0.7
14						
15	0.1	0.7	0.6	0.9	0.6	1.1
16	0.5	4.0	3.9	3.6	0.1	3.4
17	1.7	4.2	3.5	4.0	1.9	3.2
18	0.9	0.4	0.3	0.0	0.9	0.3
19	1.4	2.6	1.9	1.8	1.4	2.4
20	1.9	22.3	26.6	4.9	0.9	5.3
23	1.6	0.5	1.0	0.9		0.9
24	0.7	1.7	1.7	0.4	0.9	0.2
25	0.6	0.6	0.2	0.4	0.2	0.5
26	0.0	0.2	0.2	0.4	1.4	0.8
27						
28	8.5			2.5	33.3	3.2
29	1.3	0.1	0.7	1.1	0.9	1.2
30	0.2	0.1	0.3	0.9	1.4	1.6
31	1.7	1.6	1.8	2.7	19.6	3.0
32	5.0	4.9	20.9	8.2	40.4	8.2
33	0.0	0.3	0.2	0.4	1.7	0.1
34	0.4	1.3	0.7	0.1	0.4	0.0
35						
36	1.5	2.8	0.8	0.1	3.8	0.4
37	1.7	0.7	1.5	0.6	0.7	0.6
38	0.5	0.7	0.2	0.6	0.4	0.7
39	6.2	20.1	10.9	38.5	1.9	37.2
40						
42	0.3	1.3	1.6	1.2	0.4	0.6
43	0.0	1.8	0.9	2.3	0.9	1.4
44	0.1	1.0	0.8	0.1	0.9	1.8

45						
46	1.6	3.1	2.8	3.4	0.1	3.2
47	0.0	1.4	1.3	1.0		1.4
48						
49	3.4	1.0	0.9	1.6	3.8	1.5
50	3.0	8.6	7.0	4.6	7.7	34.7
51	3.0	1.6	0.0	2.0	2.7	1.1
52	0.4	1.4	1.2	0.9	0.9	0.9
53	1.1	1.3	0.7	1.0	2.5	1.4
54	2.8	0.0	1.5	1.6	0.7	1.7
55	0.9	1.4	0.8	1.7	0.2	1.8
56						

Table 7-3 Z-score for nitrite

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.2	4.5		1.0		2.6
2	1.5	0.6	1.1	1.4	1.4	1.4
3	0.7	0.6	1.1	1.4	0.1	0.6
4	0.2	0.4	0.9	0.6	1.2	0.2
5	0.5	1.1		0.6		0.3
6						
7	0.0	0.1	0.1	0.7	0.9	0.7
9	1.0	1.7	0.4	1.4	0.5	0.2
10	4.0	1.4	0.9	4.2	1.2	4.2
11	1.0	0.6	0.1	0.2	0.1	1.0
12	4.1	1.7		4.7		4.7
13	0.2	0.6	1.1	0.6	0.1	0.2
14	1.5	0.6	42.4	0.6	0.1	0.2
15	0.6	0.4	0.9	0.2	0.1	1.0
16	1.0	1.0	1.1	0.1	0.8	0.3
17	0.8	0.9	1.0	0.9	0.1	0.6
18	0.7	1.7	2.0	1.4	1.4	2.3
19	0.3	0.6	1.1	0.6	1.4	0.6
20	2.8	7.8		6.3		6.3
23	1.9	4.5	4.0	5.9	3.7	6.7
24	0.7	0.4	0.1	0.2	1.2	0.2
25	0.0	0.9	1.1	0.3	1.4	0.7
26	0.6	1.4	0.9	1.8	2.4	1.8
27						
28	2.4	0.4		7.1		7.9
29	0.7	0.6	1.1	0.6	1.4	0.6
30	0.2	0.4	0.1	1.8	1.2	1.0
31	2.0	0.3		0.6		0.2
32	0.6	11.6	20.6	5.9	1.4	5.9
33	0.2	4.5	5.1	1.0	6.2	1.0
34	1.5	3.4	4.0	2.6	7.5	3.4
35	2.3	1.4	0.2	1.8	0.7	3.4
36	1.1	1.4	2.0	0.6	0.1	0.6
37	2.7	1.4	1.1	1.8	1.4	1.8
38	0.3	0.6	0.1	0.6	0.1	0.6
39	0.2	8.5	8.2	1.0	8.8	2.6
40						
42	1.9	1.2	0.6	0.4	0.5	0.7
43	1.4	2.6	1.1	3.3	1.4	1.9
44	1.5	7.5	4.0	3.4	6.2	3.4

45	1.9	3.8		0.2		1.8
46	0.7	0.4	0.9	1.4	1.2	0.2
47	0.9	0.8		1.3		1.0
48						
49	4.5	10.6	13.4	10.7	16.4	11.6
50	0.7	7.5	5.1	2.3	10.0	15.3
51	1.5	3.4	5.1	5.1	3.7	6.7
52	1.1	1.7	1.1	1.4	1.4	1.4
53	0.7	0.4	0.1	0.6	1.2	0.2
54	0.2	0.4	0.1	0.6	1.2	0.2
55	0.3	0.6	1.1	0.6	0.1	0.6
56						

Table 7-4 Z-score for phosphate

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.7	6.5	0.9	1.5	1.4	1.5
2	0.8	0.5	1.1	0.3	0.5	0.1
3	0.7	0.5	0.2	0.8	0.9	0.8
4	0.5	0.3	0.6	1.3	0.5	0.1
5	0.5	1.5	1.4	0.7		0.9
6	2.6	1.4	0.6	1.5	1.5	1.8
7	0.1	0.8	1.4	0.1	0.0	0.1
9	8.6	14.2	12.8	10.1	11.3	8.7
10	0.2	1.9	1.8	0.4	0.0	0.4
11	2.6	0.3	0.4	1.3	1.0	0.8
12	1.1	5.7	5.0	2.0		2.5
13	2.0	1.6	1.4	1.3	1.5	1.5
14	1.0	0.0	5.0	0.6	1.7	0.6
15	0.4	2.2	2.0	1.5	0.0	1.7
16	0.2	6.1	6.8	4.4	1.0	4.6
17	0.7	1.0	1.2	1.7	0.2	1.2
18	0.7	1.4	1.8	0.3	0.5	0.1
19	1.9	0.5	0.9	0.1	1.4	0.1
20	1.0	1.6	1.1	1.0	2.4	1.3
23	0.8	0.8	1.3	1.3	0.5	2.4
24	2.9	0.0	0.0	3.6	1.4	2.4
25	0.3	0.3	0.3	0.7	0.5	0.1
26	1.4	1.1	0.2	1.5	0.5	2.0
27	0.8	6.6	6.1	4.1	5.9	4.1
28	4.7	1.1	0.3	1.8		1.5
29	0.8	0.0	0.3	0.4	1.0	0.1
30	0.8	6.3	6.3	2.5	1.4	2.9
31	2.0	6.3	5.8	1.7	0.0	1.0
32	16.4	15.3	1.1	12.9	1.5	12.9
33	1.3	1.4	0.2	0.8	2.9	0.6
34	6.2	7.1	4.1	3.8	1.4	4.8
35	0.2	5.2	4.9	3.3	4.4	2.6
36	1.6	9.8	10.7	4.0	0.9	4.0
37	0.1	3.5	3.8	2.4	1.0	2.2
38	1.1	0.1	0.3	0.8	1.6	0.8
39	1.6	12.3	8.0	5.0	5.9	9.6
40	0.1	0.8	0.2	0.3	0.5	0.6
42	0.8	0.5	1.0	0.8	0.3	0.9
43	3.2	10.0	6.2	3.6	0.3	3.3
44	0.7	0.8	1.6	0.6	2.4	0.3

45	1.6	1.4	0.7	0.8	3.7	0.6
46	1.4	1.1	2.7	1.1	1.0	0.6
47	9.8	51.1	32.6	16.0		15.9
48	0.7	0.3	0.5	0.6	0.9	0.6
49	6.8	3.0	0.6	4.5	14.3	4.3
50	2.9	58.4	0.3	4.3	6.9	3.8
51	0.5	1.6	1.5	0.8	1.0	1.5
52	0.2	2.5	2.5	0.8	0.0	0.8
53	1.1	2.7	2.5	0.6	0.9	1.3
54	0.8	0.8	0.5	0.3	1.0	0.3
55	0.5	0.3	0.5	0.1	0.5	0.3
56	0.4	0.3	0.0	0.3	0.9	0.8

Table 7-5 Z-score for silicate

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.3	1.7	0.5	1.1	0.8	1.0
2						
3	0.8	1.5	2.8	1.6	3.0	1.3
4	0.6	0.7	1.4	1.3	0.2	3.0
5	1.4	2.9	4.2	3.9	1.4	4.2
6	1.6	0.2	0.9	1.3	0.7	1.6
7	0.0	0.6	0.4	0.6	0.2	0.8
9	4.4	6.4	5.8	9.6	12.0	8.0
10	0.1	0.3	0.6	0.8	0.7	0.9
11						
12	1.1	1.8	2.2	1.6	1.6	2.4
13						
14	0.1	1.5	2.0	3.2	0.8	3.1
15	0.2	1.6	1.6	2.0	0.7	1.9
16	1.0	2.9	3.9	3.6	0.2	3.3
17	1.5	3.5	4.3	4.0	0.4	3.8
18	0.1	1.0	1.0	0.9	0.6	0.9
19	1.4	2.4	3.0	2.2	1.0	1.9
20	1.7	2.9	1.6	0.2	0.7	1.4
23	1.3	0.2	0.4	1.0	1.8	0.9
24	1.5	4.7	20.8	5.3	3.0	5.0
25	0.7	0.3	0.5	0.7	0.8	0.8
26	1.1	0.0	0.3	0.6	2.5	0.4
27	7.8	1.7	0.9	0.3	7.9	0.4
28						
29	1.5	0.4	0.8	4.0	1.9	3.2
30	2.5	4.7	2.6	5.4	0.7	5.7
31	0.0	1.2	1.5	1.4	0.3	2.0
32						
33	0.5	0.3	0.6	0.4	0.8	0.3
34	0.2	0.0	0.4	1.2	1.4	0.9
35	0.0	6.7	1.4	0.1	1.5	0.3
36	2.2	0.1	1.2	0.1	3.8	0.1
37	2.6	4.5	5.2	4.2	3.7	4.8
38	19.4	0.6	0.9	0.8	0.0	0.8
39	4.2	7.4	18.4	11.0	0.6	28.3
40						
42	2.9	2.3	0.5	0.7	1.6	0.7
43	0.3	1.3	0.9	0.4	3.8	0.5
44	3.0	1.6	0.7	0.5	0.1	0.3

45	0.1	0.1	0.2	1.3	1.6	1.3
46	2.0	2.6	3.1	3.9	0.3	3.3
47	1.1	1.0	0.4	0.4	1.0	1.1
48	0.5	0.2	0.4	0.4	0.2	0.4
49	0.4	3.7	4.5	1.8	0.2	1.4
50	10.5	25.6	33.5	26.9		137.0
51	0.4	0.8	2.5	2.2	1.3	2.6
52	1.6	5.5	6.8	5.1	0.0	4.9
53	1.8	1.2	1.0	2.7	4.6	0.8
54	0.7	0.9	1.2	0.6	1.9	0.5
55	0.7	1.1	1.8	2.5	1.0	2.6
56	0.5	0.1	0.3	0.0	0.1	0.3

Table 7-6 Z-score for phosphate and nitrate+nitrite

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.5	3.7	1.0	2.2	1.4	1.5
2	0.7	1.0	1.4	0.4	0.5	0.2
3	0.5	0.6	0.4	0.6	0.7	0.5
4	1.0	1.6	1.5	2.1	0.7	1.7
5	0.6	1.2	0.7	1.0		1.1
6	4.2	2.4	1.1	4.0	1.2	3.4
7	0.3	0.9	1.0	0.5	0.9	0.5
9	8.1	10.3	8.9	8.9	10.7	7.7
10	0.8	1.3	1.2	0.5	0.5	0.5
11	1.6	0.6	0.4	1.3	0.8	1.0
12	2.7	4.5	3.3	2.9		3.1
13	1.1	1.0	0.7	0.9	1.2	1.0
14	3.5	5.0	7.1	7.1	0.9	6.9
15	0.2	1.5	1.3	1.2	1.2	1.5
16	0.4	5.0	5.2	3.9	1.0	3.9
17	1.3	2.5	2.3	2.7	2.4	2.1
18	0.9	0.9	1.0	0.2	0.7	0.2
19	1.6	1.6	1.3	0.9	2.3	1.2
20	1.3	11.9	13.3	3.1	2.4	3.4
23	1.2	0.7	1.2	1.1	0.5	1.7
24	2.4	0.8	0.9	1.8	1.2	1.4
25	0.5	0.4	0.3	0.7	0.9	0.3
26	0.7	0.7	0.1	1.0	2.5	1.4
27	0.6	3.7	3.2	2.9	10.7	2.9
28	6.8	1.1	0.3	2.3	58.7	2.5
29	1.0	0.1	0.5	0.6	1.0	0.5
30	0.5	3.2	3.3	1.6	2.8	2.2
31	2.0	3.9	3.7	2.3	17.9	2.1
32	10.7	9.9	10.5	10.4	36.3	10.4
33	0.7	0.9	0.2	0.5	4.7	0.4
34	3.2	4.2	2.4	2.0	1.4	2.4
35	0.7	3.2	3.1	3.2	6.5	3.1
36	1.6	6.3	5.8	2.0	2.4	2.2
37	0.8	2.1	2.5	1.5	0.8	1.4
38	0.9	0.4	0.3	0.8	1.5	0.8
39	4.0	15.9	9.3	21.3	6.6	22.9
40						
42	0.5	0.9	1.3	0.8	0.5	0.7
43	1.7	5.8	3.5	2.8	0.6	2.2
44	0.4	0.9	1.2	0.4	1.7	1.1
45	1.3	1.0	0.7	0.7	3.7	0.7
46	1.5	2.1	2.8	2.3	1.4	1.9
47	5.0	26.3	16.9	8.4		8.5
48	0.9	0.5	0.4	0.6	0.9	0.7

49	5.4	2.1	0.8	3.2	14.0	3.0
50	3.0	33.4	3.5	4.5	12.6	19.1
51	1.7	1.6	0.8	1.4	1.9	1.3
52	0.3	1.9	1.9	0.9	0.5	0.9
53	1.1	2.0	1.6	0.9	3.4	1.4
54	1.8	0.4	0.9	1.0	0.7	1.1
55	0.7	0.8	0.6	0.8	0.5	0.9
56	0.4	0.9	1.2	0.5	0.7	1.2

Note: * means nitrate used instead of nitrate+nitrite

Table 7-7 Z-score for phosphate, nitrate+nitrite and silicate

LABNUM	sample # 1	sample #2	sample #3	sample # 4	sample # 5	sample # 6
1	0.5	3.0	0.8	1.8	1.1	1.3
2						
3	0.6	0.9	1.2	0.9	1.5	0.8
4	0.9	1.3	1.5	1.8	0.6	2.1
5	0.9	1.8	1.9	2.0		2.1
6	3.3	1.7	1.0	3.1	1.0	2.8
7	0.2	0.8	0.8	0.5	0.7	0.6
9	6.9	9.0	7.9	9.2	11.1	7.8
10	0.6	1.0	1.0	0.6	0.6	0.6
11						
12	2.1	3.6	3.0	2.5		2.9
13						
14	2.3	3.8	5.4	5.8	0.8	5.7
15	0.2	1.5	1.4	1.5	1.0	1.6
16	0.6	4.3	4.8	3.8	0.8	3.7
17	1.3	2.8	3.0	3.1	1.7	2.7
18	0.6	0.9	1.0	0.4	0.7	0.4
19	1.5	1.8	1.9	1.4	1.9	1.5
20	1.4	8.9	9.4	2.1	1.5	2.7
23	1.2	0.5	0.9	1.1	1.1	1.4
24	2.1	2.1	7.5	3.0	1.8	2.6
25	0.6	0.4	0.4	0.7	0.9	0.5
26	0.8	0.5	0.2	0.9	2.5	1.1
27	3.0	3.1	2.4	2.0	9.8	2.1
28						
29	1.1	0.2	0.6	1.7	1.3	1.4
30	1.2	3.7	3.1	2.9	2.1	3.3
31	1.3	3.0	3.0	2.0	12.0	2.1
32						
33	0.6	0.7	0.3	0.5	3.4	0.4
34	2.2	2.8	1.7	1.7	1.4	1.9
35	0.5	4.4	2.5	2.2	4.9	2.2
36	1.8	4.2	4.3	1.4	2.9	1.5
37	1.4	2.9	3.4	2.4	1.8	2.6
38	7.0	0.5	0.5	0.8	1.0	0.8
39	4.0	13.1	12.3	17.9	4.6	24.7
40						
42	1.3	1.4	1.0	0.8	0.8	0.7
43	1.2	4.3	2.6	2.0	1.7	1.6
44	1.3	1.1	1.1	0.4	1.1	0.8
45	0.9	0.7	0.5	0.9	2.7	0.9
46	1.7	2.3	2.9	2.8	1.0	2.4
47	3.7	17.8	11.4	5.7		6.0
48	0.8	0.4	0.4	0.5	0.7	0.6

49	3.7	2.6	2.0	2.7	9.4	2.5
50	5.5	30.8	13.5	12.0	12.6	58.4
51	1.3	1.3	1.3	1.7	1.7	1.7
52	0.7	3.1	3.5	2.3	0.3	2.2
53	1.4	1.7	1.4	1.5	3.8	1.2
54	1.4	0.6	1.0	0.9	1.1	0.9
55	0.7	0.9	1.0	1.4	0.7	1.5
56	0.4	0.7	0.9	0.3	0.5	0.9

Note: * means nitrate used instead of nitrate+nitrite

6. Conclusions

We used autoclaved natural seawater as a reference material for nutrient analysis in an inter-laboratory comparison study conducted during 2006, and we compared the 2006 data with data from a similar study conducted in 2003. Sample homogeneities for nitrate, phosphate, and silicate were 0.22%, 0.32%, and 0.19%, respectively. Sets of six samples were prepared covering concentration ranges of 0.1–42.4 μmol kg^{-1} for nitrate, 0.0–0.6 μmol kg^{-1} for nitrite, 0.0–3.0 μmol kg^{-1} for phosphate, and 1.7–156.1 μmol kg^{-1} for silicate. A set of samples was distributed to each of 55 laboratories in 20 countries. Results were returned by 52 laboratories in 19 countries.

Analytical precisions reported by the participating laboratories for all deteminands were generally better, by at least 50%, than the consensus standard deviations for the reported concentrations. Consensus standard deviations of sample #2 for all determinands were quite large, 5–10 times the corresponding homogeneities for sample #2 for all determinands. We suggest that in some laboratories, the non-linearity of the instruments was not corrected for effectively.

Our results indicate that variability of the in-house standards used by the participating laboratories, and the handling of the non-linearity of the instruments of the participating laboratories, were the primary sources of discrepancies in the results reported.

Our results also indicate that the non-linearity of the calibration curves for nutrient analysis was also a significant source of error, as well as the non-linear value-dependent errors.

Therefore, the use of a certified reference material that covers the full range of nutrient concentrations found in seawater, and the use of a common methodology for treatment of nutrient data, are essential to establish the global comparability of nutrient data for the world’s oceans.

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Appendix I

List of participating laboratories

Table A1 – List of participating laboratories

Lab#	Name	Affiliation	Country
1	Nurit Kress	Israel Oceanographic & Limnological Res	Israel
2	Naoki Nagai	Oceanographical Division Maizuru Marine Observatory	Japan
3	Susan Becker	Scripps Institution of Oceanography	U.S.A.
4	Jia-Zhong Zhang	Ocean Chemistry Division Atlantic Oceanographic and Meteorological Laboratory (AOML), NOAA	U.S.A.
5	Minhan Dai	State Key laboratory of Marine Environmental Science	China
6	David J Hydes	National Oceanography Centre	U.K.
7	Roger Kerouel	IFREMER	France
8	-	-	-
9	Cristopher Schmidt	Texas A&M University	U.S.A.
10	Hiromi Kasai	Hokkaido National Fisheries Research Institute, Fisheries Research Agency	Japan
11	Shinji Masuda	Marine Division, Nagasaki Marine Obsevatory	Japan
12	Anita Nybakk	Chemical laboratory Institute of Marine Research (Norway)	Norway
13	Masamitsu Kumagai	Hakodate Marine Observatory	Japan
14	E.Malcolm. S. Woodward	Plymouth Marine Laboratory	U.K.
15	Yoko Kiyomono	Seikai National Fisheries Research Institute, Fisheries Research Agency	Japan
16	Thomas Raabe	AquaEcology	Germany
17	Monika Schuett	Institute of Biogeochemistry and Marine Chemistry University of Hamburg	Germany
18	Agnès Youénou	IFREMER	France
19	Olivier Pierre-Duplessix	LERN/IFREMER	France
20	Ms Theresa M. Shammon	Marine monitoring, Government Laboratory, Department of Local Government and the Environment, Isle of Man Government.	Isle of Man, British Isles
21	-	-	-
22	-	-	-

Lab#	Name	Affiliation	Country
23	T Moutin	Laboratoire d'Ocèanographie et de Biogéochimie, Centre d'Ocèanologie de Marseille, UMR 6535 CNRS	France
24	Gwo-Ching Gong	Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University	Taiwan
25	Jan Van Ooijen	Royal N. I. O. Z. (Nethherlands Institute for Sea Research)	The Netherlands
26	Hidekazu Ota	Laboratory for Instrumentation and Analysis The General Environmental Technos Co., LTD. （KANSO TECHNOS）	Japan
27	Paul Worsfold	University of Plymouth, School of Earth, Ocean & Environmental Sciences	U.K.
28	Clemens Engelke	Scottish Environmnet Protection Agency (SEPA), Marine Chemistry	U.K.
29	Takashi Miyao	Marine Division, Global Environment and Marine Department, Japan Meteorological Agency	Japan
30	Mireille Pujo-Pay	Laboratoire Arago - CNRS	France
31	Li Yarong	Environmental Forensic and Analytical Science, Department of Environment and Conservation (NSW)	Australia
32	Sophie Leterme	School of Biological Sciences, University of Plymouth	U.K.
33	Phil Yeats	Environmental Research Division, Bedford Institute of Oceanography	Canada
34	Marguerite Blum	Monterey Bay Aquarium Research Institute	U.S.A.
35	Gi-Hoon Hong	Korea Ocean Research & Development Institute	South Korea
36	Katherine A. Krogslund	School of Oceanography, University of Washington	U.S.A.
37	Toste Tanhua	Leibenz-Institute of Marine Sciences University of Kiel	Germany
38	Akihiko Murata	Japan Agency for Marine-Earth Science and Technology (JAMSTEC)	Japan
	Kenichiro Sato	Marine Works Japan (MWJ)	

Lab#	Name	Affiliation	Country
39	Metiek Kimie Ngirchechol	University of Guam Marine Lab	U.S.A.
40	Takeshi Yoshimura	Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry	Japan
41	-	-	-
42	Ingela Dahllöf	National Environmental Research Institute, Denmark	Denmark
43	Chris Payne	University of British Columbia Earth and Ocean Sciences Department	Canada
44	Elisabete De Santis Braga	Instituto Oceanográfico da Universidade de São Paulo	Brazil
45	Marc Knockaert	MUMM – Management Unit of the North Sea Mathematical Models Dept. MUMM LABORATORY	Belgium
46	Edward Czobik	New South Wales Department of Environment and Conservation	Australia
47	Garvan O Donnell	Marine Institute	Ireland
48	Janet Barwell-Clarke	Institute of Ocean Sciences	Canada
49	Ming-Ming Jin	Laboratory for Marine Biogeochemistry and Ecosystem (LAMBS), Second Institute of Oceanography, State Oceanic Administration	China
50	Jun Sun	Key Laboratory of Marine Ecology & Environmental Science Institute of Oceanology, Chinese Academy of Sciences	China
51	Jianming Pan	The Second Institute of Oceanography, SOA, China	China
52	Hiroshi Ogawa	Ocean Research Institute, The University of Tokyo	Japan
53	Günther Nausch	Department of Marine Chemistry, Leibniz-Institute for Baltic Sea Research	Germany
54	Stephen C. Coverly	Bran+Luebbe	Germany
55	Kazuhiro Saito	Kobe Marine Observatory	Japan
56	Linda White	Institute of Ocean Science – Arctic research	Canada

Table A2 Cross reference table of lab# between 2006 I/C in and 2003 I/C

Lab#	RMNS Inter-comparison study 2003*
1	2
2	10
3	3
4	
5	1
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*：Laboratory# of 2003 Inter-comparison study

Appendix II

Results submitted by participating laboratories

Table A3. Results reported by the participants

2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
1																					
	1	2006	12	11	22	0.51	0.01	2	0.63	0.01	2	5.74		2	6.38	0.22	2		30.5	0.60	2
	2	2006	12	11	22	2.76	0.23	2	0.14	0.01	2	33.9		2	34.1	0.09	2		159.4	1.64	2
	3	2006	12	11	22	2.99	0.11	2	<0.08		5	43.2		2	43.2	0.12	2		136.2	2.24	2
	4	2006	12	11	22	1.65	0.16	2	0.36	0.01	2	22.6		2	23.0	1.43	2		59.8	1.46	2
	5	2006	12	11	22	0.06	0.01	2	<0.08		5	<0.08		5	<0.08		5		1.46	0.07	2
	6	2006	12	11	22	1.65	0.16	2	0.38	0.01	2	22.1		2	22.5	0.62	2		59.7	1.81	2
2																					
	1	2006	11	4	26.9	0.46	0.00	2	0.59	0.00	2			9	6.19	0.03	2				9
	2	2006	11	4	26.9	2.54	0.00	2	0.09	0.00	2			9	33.05	0.03	2				9
	3	2006	11	4	26.9	3.08	0.00	2	0.00	0.00	2			9	41.25	0.03	2				9
	4	2006	11	4	26.9	1.60	0.00	2	0.33	0.00	2			9	21.86	0.03	2				9
	5	2006	11	4	26.9	0.02	0.00	2	0.00	0.00	2			9	0.01	0.03	2				9
	6	2006	11	4	26.9	1.59	0.00	2	0.33	0.00	2			9	21.93	0.03	2				9
3																					
	1	2006	11	22	23.5	0.51	0.02	2	0.61	0.01	2	5.67	0.05	2	6.28	0.05	2	98.6	31	0.1	2
	2	2006	11	22	23.5	2.54	0.02	2	0.09	0.01	2	33.28	0.05	2	33.37	0.05	2	98.6	159	0.1	2
	3	2006	11	22	23.5	3.04	0.02	2	0.00	0.01	2	42.08	0.05	2	42.08	0.05	2	98.6	139.8	0.1	2
	4	2006	11	22	23.5	1.62	0.02	2	0.33	0.01	2	21.55	0.05	2	21.88	0.05	2	98.6	60.2	0.1	2
	5	2006	11	22	23.5	0.05	0.02	2	0.01	0.01	2	0	0.05	2	0.01	0.05	2	98.6	2.3	0.1	2
	6	2006	11	22	23.5	1.62	0.02	2	0.34	0.01	2	21.58	0.05	2	21.92	0.05	2	98.6	60	0.1	2
4																					
	1	2006	9	25	23	0.47	0.004	6	0.63	0.01	6	5.97	0.04	6	6.6	0.04	6	100	30.82	0.23	6
	2	2006	9	25	23	2.53	0.01	6	0.1	0.004	6	34.89	0.23	6	34.99	0.23	6	100	157.33	1.69	6
	3	2006	9	25	23	3.06	0.01	6	0.02	0.004	6	44.13	0.4	6	44.15	0.03	6	100	137.52	0.95	6
	4	2006	9	25	23	1.64	0.01	6	0.34	0.004	6	22.63	0.21	6	22.98	0.2	6	100	59.96	0.42	6
	5	2006	9	25	23	0.02	0.004	6	0.02	0.00	6	0	0	6	0	0	6	100	1.6	0.02	6
	6	2006	9	25	23	1.59	0.01	6	0.35	0.004	6	22.76	0.07	6	23.11	0.07	6	100	61.37	0.39	6
5																					
	1	2006	12	6		0.470	0.01	2	0.614	0.01	2	5.557	0.014	2	6.171	0.014	2		31.613	0.152	2
	2	2006	12	6		2.464	0.009	2	0.107	0.001	2	33.172	0.087	2	33.279	0.087	2		162.130	0.046	2
	3	2006	12	6		2.972	0.010	2			5	42.365	0.071	2	42.365	0.071	2		141.881	0.079	2
	4	2006	12	6		1.554	0.004	2	0.348	0.001	2	21.201	0.048	2	21.541	0.048	2		62.179	0.484	2
	5	2006	12	6				5			5			5			5		1.941	0.008	2
	6	2006	12	6		1.547	0.006	2	0.344	0.004	2	21.213	0.059	2	21.557	0.059	2		62.420	0.927	2

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued)

2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
6																					
	1	2006	11	16	22	0.40	0.04	6			9			9	5.2	0.1	6		28.4	0.6	6
	2	2006	11	16	22	2.47	0.08	6			9			9	32.2	0.6	6		155.2	7.8	6
	3	2006	11	16	22	3.06	0.09	6			9			9	41.4	0.8	6		134.0	6.7	6
	4	2006	11	16	22	1.52	0.06	6			9			9	19.8	0.4	6		57.8	1.2	6
	5	2006	11	16	22	0.00	0.03	6			9			9	0.0	0.1	6		1.5	0.0	6
	6	2006	11	16	22	1.51	0.06	6			9			9	20.3	0.4	6		57.5	1.2	6
7																					
	1	2006	10	31		0.49	0.005	2	0.626	0.005	2	5.58	0.05	2	6.21	0.05	2		30.2	0.1	2
	2	2006	10	31		2.49	0.01	2	0.095	0.003	2	33.2	0.1	2	33.3	0.1	2		157	1	2
	3	2006	10	31		2.97	0.01	2	0.012	0.003	2	42.0	0.1	2	42.0	0.1	2		136	1	2
	4	2006	10	31		1.59	0.01	2	0.357	0.005	2	21.3	0.1	2	21.7	0.1	2		59.4	0.2	2
	5	2006	10	31		0.030	0.004	2	0.018	0.003	2	0.04	0.03	2	0.06	0.03	2		1.69	0.05	2
	6	2006	10	31		1.59	0.01	2	0.357	0.005	2	21.3	0.1	2	21.7	0.1	2		59.5	0.1	2
9																					
	1	2006	11	10		0.77		2	0.650		2	7.14		2	7.78		2		34.88		2
	2	2006	11	10		3.04		2	0.113		2	36.39		2	36.50		2		169.95		2
	3	2006	11	10		3.60		2	0.015		2	46.02		2	46.04		2		144.39		2
	4	2006	11	10		2.02		2	0.365		2	24.31		2	24.68		2		66.98		2
	5	2006	11	10		0.26		2	0.015		2	0.22		2	0.24		2		4.26		2
	6	2006	11	10		1.96		2	0.350		2	23.97		2	24.32		2		65.62		2
10																					
	1	2006	10	5		0.48	0.03	6	0.72	0.02	6	5.4	0.2	6			9	>98.5	30.0	0.2	6
	2	2006	10	5		2.45	0.04	6	0.11	0.01	6	33.3	0.3	6			9	>98.5	156.4	0.5	6
	3	2006	10	5		2.95	0.03	6	0.02	0.01	6	42.0	0.4	6			9	>98.5	136.3	0.4	6
	4	2006	10	5		1.57	0.03	6	0.40	0.01	6	21.4	0.2	6			9	>98.5	59.5	0.2	6
	5	2006	10	5		0.03	0.02	6	0.02	0.01	6	0.0	0.0	6			9	>98.5	1.5	0.2	6
	6	2006	10	5		1.57	0.03	6	0.40	0.01	6	21.4	0.3	6			9	>98.5	59.6	0.2	6
11																					
	1	2006	10	1	25	0.40	0.01	2	0.65	0.00	2	5.79	0.03	2	6.44	0.03	2	100			9
	2	2006	10	1	25	2.51	0.02	2	0.09	0.00	2	33.98	0.05	2	34.07	0.05	2	100			9
	3	2006	10	1	25	3.05	0.01	2	0.01	0.00	2	42.70	0.08	2	42.71	0.08	2	100			9
	4	2006	10	1	25	1.53	0.01	2	0.35	0.00	2	22.09	0.10	2	22.44	0.10	2	100			9
	5	2006	10	1	25	0.01	0.01	2	0.01	0.00	2	0.00	0.02	2	0.01	0.02	2	100			9
	6	2006	10	1	25	1.55	0.01	2	0.36	0.00	2	22.05	0.05	2	22.40	0.05	2	100			9

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued) 2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
12																					
	1	2006	9	22	20	0.45	0.04	2	0.53	0.04	2	5.0	0.4	2	5.5	0.4	2		29.0	0.2	2
	2	2006	9	22	20	2.31	0.04	2	0.08	0.04	2	32.2	0.4	2	32.3	0.4	2		151.7	0.2	2
	3	2006	9	22	20	2.81	0.04	2			5	41.2	0.4	2	41.3	0.4	2		131.9	0.2	2
	4	2006	9	22	20	1.50	0.04	2	0.29	0.04	2	20.4	0.4	2	20.7	0.4	2		57.5	0.2	2
	5	2006	9	22	20			5			5			5			5		1.3	0.2	2
	6	2006	9	22	20	1.48	0.04	2	0.29	0.04	2	20.4	0.4	2	20.7	0.4	2		56.8	0.2	2
13																					
	1	2006	10	11	22.9	0.42	0.01	2	0.63	0.00	2	5.75	0.00	2	6.37	0.00	2	99			9
	2	2006	10	11	22.9	2.46	0.01	2	0.09	0.00	2	33.77	0.02	2	33.86	0.02	2	99			9
	3	2006	10	11	22.9	2.97	0.01	2	0.00	0.00	2	42.48	0.03	2	42.48	0.03	2	99			9
	4	2006	10	11	22.9	1.53	0.01	2	0.34	0.00	2	21.82	0.00	2	22.16	0.01	2	99			9
	5	2006	10	11	22.9	0.00	0.00	2	0.01	0.00	2	0.00	0.00	2	0.00	0.00	2	99			9
	6	2006	10	11	22.9	1.52	0.01	2	0.35	0.00	2	21.83	0.01	2	22.18	0.01	2	99			9
14																					
	1	2006	12	14		0.52	0.02	2	0.59	0.00	2			9	5.18	0.01	2		30.08	0.05	2
	2	2006	12	14		2.52	0.02	2	0.09	0.00	2			9	29.37	0.10	2		158.95	0.00	2
	3	2006	12	14		2.81	0.02	2	0.42	0.00	2			9	36.02	0.00	2		138.49	0.44	2
	4	2006	12	14		1.56	0.02	2	0.34	0.01	2			9	17.32	0.08	2		61.60	0.00	2
	5	2006	12	14		0.065	0.005	2	0.01	0.00	2			9	0.02	0.00	2		1.82	0.00	2
	6	2006	12	14		1.56	0.01	2	0.35	0.00	2			9	17.46	0.05	2		61.46	0.05	2
15																					
	1	2006	10	23-27		0.50	0.01	6	0.64	0.01	6	5.67	0.06	6	6.31	0.06	6		29.91	0.29	6
	2	2006	10	23-27		2.60	0.04	6	0.10	0.00	6	33.27	0.47	6	33.38	0.47	6		152.1	2.8	6
	3	2006	10	23-27		3.12	0.05	6	0.02	0.00	6	41.99	0.49	6	42.01	0.49	6		132.9	1.5	6
	4	2006	10	23-27		1.65	0.02	6	0.35	0.01	6	21.31	0.18	6	21.66	0.18	6		57.2	1.3	6
	5	2006	10	23-27		0.03	0.01	6	0.01	0.01	6	0.06	0.01	6	0.07	0.01	6		1.79	0.04	6
	6	2006	10	23-27		1.66	0.03	6	0.36	0.01	6	21.24	0.11	6	21.60	0.11	6		57.3	0.71	6
16																					
	1	2006	10	12	20	0.4693	0.0043	6	0.6183	0.0026	6	5.5092	0.0261	6	6.1274	0.0279	6	96	29.7157	0.0873	6
	2	2006	10	12	20	2.6138	0.0168	6	0.0824	0.0082	6	33.6267	0.1461	6	33.7091	0.1497	6	96	154.4801	0.2336	6
	3	2006	10	12	20	3.1759	0.0146	6	0.0005	0.0037	6	42.9368	0.1761	6	42.9310	0.1734	6	96	134.7864	0.2239	6
	4	2006	10	12	20	1.6933	0.0017	6	0.3323	0.0018	6	21.7138	0.1117	6	22.0461	0.1120	6	96	58.9895	0.0463	6
	5	2006	10	12	20	0.0097	0.0069	6	0.0043	0.0143	6	0.0375	0.0332	6	0.0418	0.0417	6	96	1.6053	0.0265	6
	6	2006	10	12	20	1.7012	0.0051	6	0.3345	0.0090	6	21.6510	0.0635	6	21.9854	0.0699	6	96	58.7561	0.2441	6

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued) 2006 RMNS Intercomparison Exercise

I A	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
17																					
	1	2006	10	16		0.5099	0.0156	2	0.6455	0.0018	2	6.0181		2	6.6637	0.1119	2		31.7353	0.4674	2
	2	2006	10	16		2.5555	0.0185	2	0.1055	0.0012	2	35.3625		2	35.4680	0.1288	2		163.3687	0.0893	2
	3	2006	10	16		3.0876	0.0100	2	0.0205	0.0044	2	44.7860		2	44.8066	0.1800	2		142.1318	0.0923	2
	4	2006	10	16		1.6585	0.0124	2	0.3585	0.0029	2	22.9179		2	23.2764	0.1880	2		62.2116	0.0895	2
	5	2006	10	16		0.0261	0.0033	2	0.0101	0.0020	2	0.1084		2	0.1185	0.0014	2		1.7252	0.1696	2
	6	2006	10	16		1.6385	0.0130	2	0.3546	0.0014	2	22.6693		2	23.0240	0.1164	2		62.0710	0.1495	2
18																					
	1	2006	11	23		0.51		2	0.61		2	5.51		2	6.12		2		30.3		2
	2	2006	11	23		2.47		2	0.08		2	33.4		2	33.5		2		158		2
	3	2006	11	23		2.95		2	0.03		2	42.2		2	42.3		2		137		2
	4	2006	11	23		1.6		2	0.33		2	21.6		2	22.0		2		59.6		2
	5	2006	11	23		0.04		2	0		2	0		2	0		2		1.77		2
	6	2006	11	23		1.59		2	0.32		2	21.7		2	22.1		2		59.6		2
19																					
	1	2006	11	23		0.55	0.02	2	0.62	0.01	2	5.95	0.1	2	6.57	0.1	2		31.6	0.1	2
	2	2006	11	23		2.54	0.02	2	0.09	0.01	2	34.7	0.1	2	34.8	0.1	2		161	1	2
	3	2006	11	23		3.07	0.02	2	0.00	0.01	2	43.7	0.1	2	43.7	0.1	2		140	1	2
	4	2006	11	23		1.58	0.02	2	0.34	0.01	2	22.2	0.1	2	22.6	0.1	2		60.7	0.1	2
	5	2006	11	23		0.06	0.02	2	0.00	0.01	2	0.09	0.1	2	0.09	0.1	2		1.87	0.1	2
	6	2006	11	23		1.58	0.02	2	0.34	0.01	2	22.4	0.1	2	22.8	0.1	2		60.5	0.1	2
20																					
	1	2006	11	16-21	19.4	0.52	0.02	2	0.56	0.01	2	6.05		2	6.61	0.07	2	102	28.36	1.43	2
	2	2006	11	16-21	19.4	2.58	0.02	2	0.02	0.01	2	24.15		2	24.17	0.05	2	102	149.27	1.45	2
	3	2006	11	16-21	19.4	3.08	0.02	2			5	24.50		2	24.50	0.04	2	102	132.86	0.03	2
	4	2006	11	16-21	19.4	1.63	0.04	2	0.27	0.00	2	19.96		2	20.23	0.10	2	102	58.69	1.20	2
	5	2006	11	16-21	19.4	0.08	0.02	2			5	0.00		2			5	102	1.50	0.01	2
	6	2006	11	16-21	19.4	1.64	0.02	2	0.27	0.00	2	19.85		2	20.12	0.04	2	102	57.72	0.52	2
23																					
	1					0.46	0.02	2	0.67	0.05	2	6	0.1	2			9		28.8	0.1	2
	2					2.55	0.03	2	0.14	0.03	2	33.8	0.8	2			9		155.3	0.3	2
	3					3.09	0.02	2	0.05	0.01	2	41.7	1.2	2			9		134.8	0.4	2
	4					1.64	0.03	2	0.42	0.01	2	21.9	0.9	2			9		58	0.3	2
	5					0.04	0.03	2	0.04	0.01	2	<DL		5			9		1.25	0.02	2
	6					1.69	0.03	2	0.43	0.02	2	21.9	0.8	2			9		58.1	0.4	2

Flag 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued)

2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
24																					
	1	2006	10	5	25.8	0.58		2	0.61		2	5.83	0.01	2	6.70	0.01	2		31.7		2
	2	2006	10	5	25.8	2.52		2	0.10		2	32.88	0.08	2	33.02	0.08	2		145.3	0.5	2
	3	2006	10	5	25.8	3.03		2	0.01		2	41.24	0.09	2	41.25	0.09	2		167.9	0.2	2
	4	2006	10	5	25.8	1.74		2	0.35		2	21.48	0.05	2	21.97	0.05	2		63.3		2
	5	2006	10	5	25.8	0.06		2	0.02		2	0.00	0.00	2	0.00	0.00	2		2.3		2
	6	2006	10	5	25.8	1.69		2	0.35		2	21.65	0.07	2	22.15	0.07	2		63.1		2
25																					
	1	2006	12	12	21.8	0.474	0.02	2	0.626	0.015	2	5.56	0.26	2	6.19	0.25	2	99	29.36	0.5	2
	2	2006	12	12	21.8	2.509	0.02	2	0.105	0.015	2	33.35	0.26	2	33.46	0.25	2	99	156.3	1.0	2
	3	2006	12	12	21.8	3.018	0.02	2	0.022	0.015	2	42.24	0.26	2	42.27	0.25	2	99	134.5	1.0	2
	4	2006	12	12	21.8	1.554	0.02	2	0.351	0.015	2	21.46	0.26	2	21.81	0.25	2	99	58.23	0.5	2
	5	2006	12	12	21.8	0.020	0.02	2	0.022	0.015	2	0.03	0.26	2	0.05	0.25	2	99	1.47	0.5	2
	6	2006	12	12	21.8	1.588	0.02	2	0.356	0.015	2	21.44	0.26	2	21.8	0.25	2	99	58.19	0.5	2
26																					
	1	2006	12	22		0.44	0.00	2	0.64	0.00	2	5.68	0.04	2	6.32	0.04	2		28.99	0.19	2
	2	2006	12	22		2.48	0.01	2	0.11	0.00	2	33.48	0.04	2	33.59	0.04	2		155.64	0.14	2
	3	2006	12	22		3.04	0.00	2	0.02	0.00	2	42.51	0.04	2	42.54	0.04	2		135.89	0.38	2
	4	2006	12	22		1.52	0.00	2	0.37	0.00	2	21.45	0.01	2	21.82	0.01	2		58.38	0.21	2
	5	2006	12	22		0.02	0.01	2	0.03	0.00	2	0.09	0.00	2	0.12	0.00	2		1.10	0.16	2
	6	2006	12	22		1.50	0.02	2	0.37	0.00	2	21.34	0.03	2	21.71	0.03	2		58.52	0.25	2
27																					
	1	2006	11	15		0.46	0.05	2			9			9	6.41	0.05	2		38.4	0.8	2
	2	2006	11	15		2.28	0.20	2			9			9	34.1	0.6	2		152	1	2
	3	2006	11	15		2.76	0.16	2			9			9	42.7	0.5	2		134	1	2
	4	2006	11	15		1.41	0.19	2			9			9	22.6	0.5	2		58.6	0.7	2
	5	2006	11	15		0.15	0.07	2			9			9	0.36	0.05	2		3.37	0.26	2
	6	2006	11	15		1.41	0.20	2			9			9	22.6	0.5	2		58.5	0.6	2
28																					
	1	2006	10	18		0.33	0.02	2	0.57	0.03	2	4.04	0.18	2	4.60	0.21	2				9
	2	2006	10	18		2.56	0.12	2	0.10	0.00	2			9			9				9
	3	2006	10	18		3.02	0.14	2			9			9			9				9
	4	2006	10	18		1.51	0.07	2	0.26	0.01	2	20.78	0.95	2	21.04	0.96	2				9
	5	2006	10	18				9			9	1.30	0.06	2	1.30	0.06	2				9
	6	2006	10	18		1.52	0.07	2	0.25	0.01	2	20.55	0.94	2	20.81	0.95	2				9

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued)

2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
29																					
	1	2006	10	24	23.5	0.46	0.01	2	0.61	0	2	5.93	0.02	2	6.54	0.02	2	100	31.73	0.01	2
	2	2006	10	25	22.6	2.52	0	2	0.09	0	2	33.54	0.03	2	33.62	0.02	2	100	156.62	0.14	2
	3	2006	10	25	23	3.02	0	2	0	0	2	41.91	0.03	2	41.92	0.02	2	100	136.66	0.02	2
	4	2006	10	26	24.9	1.57	0	2	0.34	0	2	21.96	0.02	2	22.3	0.02	2	100	62.22	0.17	2
	5	2006	10	26	26.2	0.01	0.01	2	0	0	2	0	0.01	2	0	0.01	2	100	2.05	0.03	2
	6	2006	10	27	25.1	1.58	0.01	2	0.34	0	2	21.99	0.03	2	22.33	0.03	2	100	61.58	0.03	2
30																					
	1	2006	11	7	20.6	0.46	0.00	2	0.63	0.01	2	5.64	0.05	2	6.27	0.05	2		27.5	0.1	2
	2	2006	11	8	21.8	2.29	0.01	2	0.10	0.00	2	33.61	0.09	2	33.71	0.09	2		166.1	0.7	3
	3	2006	11	8	21.8	2.75	0.03	2	0.01	0.00	2	42.23	0.11	2	42.24	0.11	2		139.5	0.5	3
	4	2006	11	8	19.6	1.48	0.01	2	0.37	0.00	2	21.91	0.18	2	22.28	0.18	2		63.4	0.0	3
	5	2006	11	7	20.6	0.06	0.01	2	0.02	0.00	2	0.09	0.00	2	0.11	0.00	2		1.5	0.0	2
	6	2006	11	8	21	1.46	0.01	2	0.36	0.00	2	22.12	0.02	2	22.48	0.02	2		63.7	0.3	3
31																					
	1	2006	11	2		0.42		2	0.58		2	5.36		2	5.94		2		30.1		2
	2	2006	11	2		2.75		2	0.093		2	32.9		2	33.0		2		153		2
	3	2006	11	2		3.29		2			5	41.2		2	41.3		2		133		2
	4	2006	11	2		1.66		2	0.34		2	20.7		2	21.0		2		57.7		2
	5	2006	11	2		0.03		2			5	0.78		2	0.80		2		1.70		2
	6	2006	11	2		1.63		2	0.35		2	20.6		2	20.9		2		57.2		2
32																					
	1	2006	11	15	20	1.03	0.10	2	0.64	0.21	2	4.72	0.16	2	5.36	0.37	2				9
	2	2006	11	15	20	3.08	0.10	2	0.21	0.21	2	31.49	0.16	2	31.71	0.37	2				9
	3	2006	11	15	20	3.08	0.10	2	0.21	0.21	2	28.34	0.16	2	28.55	0.37	2				9
	4	2006	11	15	20	1.03	0.10	2	0.42	0.21	2	18.89	0.16	2	19.32	0.37	2				9
	5	2006	11	15	20	0.00	0.10	2	0.00	0.21	2	1.57	0.16	2	1.57	0.37	2				9
	6	2006	11	15	20	1.03	0.10	2	0.42	0.21	2	18.89	0.16	2	19.32	0.37	2				9
33																					
	1	2006	9	18		0.53	0.01	6	0.63	0.00	6	5.69	0.04	6	6.32	0.04	6		29.64	0.09	6
	2	2006	9	18		2.57	0.03	6	0.14	0.00	6	33.70	0.09	6	33.84	0.08	6		155.17	0.44	6
	3	2006	9	18		3.04	0.04	6	0.06	0.00	6	42.51	0.34	6	42.57	0.33	6		134.44	1.23	6
	4	2006	9	18		1.55	0.02	6	0.36	0.00	6	21.73	0.13	6	22.09	0.13	6		59.21	0.62	6
	5	2006	9	18		0.09	0.005	6	0.06	0.00	6	0.10	0.03	6	0.16	0.03	6		1.81	0.06	6
	6	2006	9	18		1.56	0.02	6	0.36	0.00	6	21.58	0.02	6	21.94	0.02	6		58.59	0.03	6

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued)

2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
34																					
	1	2006	9	25	20.5	0.28	0.02	2	0.66	0.01	2	5.61	0.01	2	6.29	0.02	2	96	30.33	0.22	2
	2	2006	9	25	20.5	2.26	0.05	2	0.13	0.01	2	33.03	0.02	2	33.17	0.03	2	96	155.76	0.62	2
	3	2006	9	25	20.5	2.85	0.07	2	0.05	0.01	2	41.94	0.02	2	41.99	0.03	2	96	136.00	1.09	2
	4	2006	9	25	20.5	1.42	0.05	2	0.38	0.01	2	21.64	0.04	2	22.04	0.05	2	96	59.90	0.42	2
	5	2006	9	25	20.5	0.06	0.05	2	0.07	0.02	2	0.02	0.01	2	0.05	0.02	2	96	1.96	0.05	2
	6	2006	9	25	20.5	1.38	0.04	2	0.39	0.00	2	21.61	0.08	2	22.02	0.08	2	96	59.59	0.33	2
35																					
	1	2006	11	13		0.48	0.05	2	0.68	0.01	2			9	6.56	0.40	2		30.14	0.39	2
	2	2006	11	13		2.71	0.05	2	0.11	0.01	2			9	34.23	0.18	2		141.03	1.78	2
	3	2006	11	13		3.25	0.03	2	0.013	0.006	2			9	43.31	0.71	2		133.22	1.39	2
	4	2006	11	13		1.73	0.03	2	0.37	0.01	2			9	23.08	0.85	2		58.78	0.99	2
	5	2006	11	13		0.12	0.01	2	0.016	0.006	2			9	0.21	0.04	2		1.32	0.02	2
	6	2006	11	13		1.70	0.06	2	0.39	0.01	2			9	23.20	0.49	2		58.59	0.57	2
36																					
	1	2006	12	15		0.54		2	0.60		2	5.97		2			9		27.82		2
	2	2006	12	15		2.88		2	0.11		2	34.76		2			9		155.59		2
	3	2006	12	15		3.51		2	0.03		2	41.84		2			9		137.21		2
	4	2006	12	15		1.76		2	0.34		2	21.58		2			9		58.95		2
	5	2006	12	15		0.05		2	0.01		2	0.18		2			9		2.48		2
	6	2006	12	15		1.76		2	0.34		2	21.72		2			9		58.93		2
37																					
	1	2006	12	5	30	0.49	0	6	0.69	0	6	5.35	0.02	6	6.03	0.02	6	100	27.39	0.02	6
	2	2006	12	5	30	2.65	0.01	6	0.11	0.01	6	33.87	0.1	6	33.97	0.1	6	100	145.72	0.23	6
	3	2006	12	5	30	3.2	0	6	0	0	6	43.38	0.12	6	43.38	0.12	6	100	127.18	0.16	6
	4	2006	12	5	30	1.69	0.01	6	0.37	0	6	21.41	0.06	6	21.78	0.06	6	100	55.3	0.17	6
	5	2006	12	5	30	0.01	0.01	6	0	0	6	0.01	0.02	6	0.01	0.02	6	100	0.83	0.08	6
	6	2006	12	5	30	1.68	0.01	6	0.37	0.01	6	21.4	0.02	6	21.76	0.02	6	100	54.79	0.04	6
38																					
	1	2006	10	21	26.4	0.523		2	0.62		2	5.58		2	6.20		2		9.53		2
	2	2006	10	21	26.4	2.523		2	0.09		2	33.28		2	33.37		2		154.33		2
	3	2006	10	21	26.4	3.018		2	0.01		2	42.26		2	42.27		2		133.98		2
	4	2006	10	21	26.4	1.622		2	0.34		2	21.39		2	21.73		2		58.18		2
	5	2006	10	21	26.4	0.063		2	0.01		2	0.05		2	0.05		2		1.64		2
	6	2006	10	21	26.4	1.619		2	0.34		2	21.38		2	21.72		2		58.15		2

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued) 2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
39																					
	1	2006	11	10		0.54		2	0.63		2	4.48		2	5.11		2		25.67		2
	2	2006	11	10		2.97		2	0.18		2	25.08		2	25.26		2		139.32		2
	3	2006	11	10		3.39		2	0.09		2	35.02		2	35.11		2		106.48		2
	4	2006	11	10		1.80		2	0.36		2	8.79		2	9.15		2		49.53		2
	5	2006	11	10		0.15		2	0.08		2	0.11		2	0.18		2		1.78		2
	6	2006	11	10		2.00		2	0.38		2	9.23		2	9.61		2		34.93		2
40																					
	1	2006	12	5	24	0.49	0.01	2			9			9			9				9
	2	2006	12	5	24	2.55	0.02	2			9			9			9				9
	3	2006	12	5	24	3.04	0.03	2			9			9			9				9
	4	2006	12	7	24	1.60	0.01	2			9			9			9				9
	5	2006	12	7	24	0.02	0.00	2			9			9			9				9
	6	2006	12	7	24	1.61	0.01	2			9			9			9				9
42																					
	1					0.46	0.004	2	0.67	0.004	2	5.62	0.038	2	6.29	0.041	2		27.11	0.191	2
	2					2.54	0.013	2	0.084	0.002	2	34.13	0.413	2	34.22	0.413	2		150.6	0.174	2
	3					3.078	0.025	2	0.017	0.001	2	43.5	0.091	2	43.6	0.09	2		134.6	1.26	2
	4					1.62	0.005	2	0.353	0.001	2	22	0.118	2	22.3	0.041	2		59.45	0.187	2
	5					0.024	0.015	2	0.015	0.002	2	0.02	0.046	2	0.034	0.048	2		1.99	0.042	2
	6					1.626	0.007	2	0.356	0.002	2	21.8	0.37	2	22.15	0.37	2		59.42	0.071	2
43																					
	1	2007	1	10		0.591	0.050	6	0.592	0.030	6	5.688	0.200	6	6.280	0.200	6		30.480	0.500	6
	2	2007	1	10		2.887	0.050	6	0.071	0.030	6	34.338	0.200	6	34.410	0.200	6		152.862	0.500	6
	3	2007	1	10		3.308	0.050	6	0.000	0.030	6	43.031	0.200	6	43.031	0.200	6		133.916	0.500	6
	4	2007	1	10		1.740	0.050	6	0.307	0.030	6	22.359	0.200	6	22.666	0.200	6		59.207	0.500	6
	5	2007	1	12		0.025	0.010	6	0.000	0.030	6	0.000	0.050	6	0.000	0.050	6		2.466	0.200	6
	6	2007	1	10		1.726	0.050	6	0.325	0.030	6	22.049	0.200	6	22.374	0.200	6		58.475	0.500	6
44																					
	1	2006	12	1		0.51	0.02	2	0.66	0.03	2	5.67	0.09	2			9		26.96	0.35	2
	2	2006	12	1		2.55	0.08	2	0.17	0.02	2	33.16	0.19	2			9		152.21	0.18	2
	3	2006	12	1		2.96	0.01	2	0.05	0.01	2	41.86	0.23	2			9		134.19	2.64	2
	4	2006	12	1		1.56	0.02	2	0.39	0.02	2	21.55	0.15	2			9		59.25	1.58	2
	5	2006	12	1		0.08	0.01	2	0.06	0.01	2	0.07	0.02	2			9		1.63	0.11	2
	6	2006	12	1		1.60	0.06	2	0.39	0.02	2	20.99	0.19	2			9		58.64	0.35	2

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued)

2006 RMNS Intercomparison Exercise

LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
45																					
	1	2006	10	31	22	0.54	0.06	2	0.67	0.09	2			9	6.5	0.85	2		30		2
	2	2006	10	31	22	2.57		2	0.134	0.02	2			9	34		2		156		2
	3	2006	10	31	22	3.00		2	<0.06		5			9	42		2		135		2
	4	2006	10	31	22	1.62	0.18	2	0.35	0.05	2			9	21.8	2.83	2		60		2
	5	2006	10	31	22	0.106	0.01	2	<0.06		5			9	<0.24		5		2.0	0.54	2
	6	2006	10	31	22	1.61	0.18	2	0.37	0.05	2			9	21.7	2.82	2		60		2
46																					
	1	2006	12	19	24.5	0.44	0.06	2	0.61	0.1	2	5.38	0.28	2	5.99	0.21	2		28.05	1.39	2
	2	2006	12	19	24.5	2.48	0.12	2	0.10	0.1	2	32.26	0.49	2	32.36	0.49	2		149.97	6.96	2
	3	2006	12	19	24.5	2.91	0.16	2	0.02	0.1	2	40.51	0.63	2	40.53	0.63	2		130.54	6.26	2
	4	2006	12	19	24.5	1.54	0.09	2	0.33	0.1	2	20.47	0.42	2	20.80	0.35	2		55.56	2.78	2
	5	2006	12	19	24.5	0.01	0.06	2	0.02	0.1	2	0.04	0.14	2	0.06	0.14	2		1.59	0.17	3
	6	2006	12	19	24.5	1.56	0.09	2	0.35	0.1	2	20.54	0.42	2	20.89	0.35	2		56.08	2.78	2
47																					
	1				16.5	0.810		2	0.604		2	5.687		2	6.292		2		28.937		2
	2				16.5	4.394		2	0.088		2	34.191		2	34.297		2		157.938		2
	3				16.5	4.481		2			5	43.275		2	43.275		2		135.913		2
	4				16.5	2.274		2	0.332		2	21.925		2	22.257		2		58.532		2
	5				16.5			5			5			5			5		1.428		2
	6				16.5	2.271		2	0.336		2	22.070		2	22.406		2		57.956		2
48																					
	1	2006	10	18	24.8	0.51	0.002	6			9			9	6.1	0.03	6		29.6	0.07	6
	2	2006	10	18	24.8	2.51	0.005	6			9			9	33.4	0.03	6		155.3	0.07	6
	3	2006	10	18	24.8	3.01	0.004	6			9			9	42.2	0.03	6		134.8	0.00	6
	4	2006	10	18	24.8	1.61	0.002	6			9			9	21.8	0.03	6		58.5	0.07	6
	5	2006	10	18	24.8	0.05	0.000	6			9			9	0.0	0.01	6		1.6	0.07	6
	6	2006	10	18	24.8	1.61	0.000	6			9			9	21.7	0.10	6		58.5	0.00	6
49																					
	1	2006	12	6	17	0.71	0.02	6	0.73	0.01	6			9	6.35	0.10	6	98	30.62	0.27	6
	2	2006	12	6	17	2.63	0.02	6	0.20	0.01	6			9	33.99	0.29	6	98	163.99	0.42	6
	3	2006	12	6	17	3.06	0.02	6	0.14	0.02	6			9	43.03	0.35	6	98	142.38	0.28	6
	4	2006	12	6	17	1.78	0.02	6	0.48	0.01	6			9	22.14	0.19	6	98	60.40	0.57	6
	5	2006	12	6	17	0.32	0.01	6	0.14	0.02	6			9	0.18	0.04	3	98	1.68	0.06	6
	6	2006	12	6	17	1.77	0.01	6	0.49	0.01	6			9	22.10	0.22	6	98	60.06	0.32	6

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued) — 2006 RMNS Intercomparison Exercise

I A	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
50																					
	1	2006	10	16	23.2	0.58	0.01	2	0.61	0.02	2	5.10	0.02	2	5.71	0.03	2		41.35	0.55	2
	2	2006	10	16	23.2	0.38	0.01	2	0.17	0.01	2	29.93	0.44	2	30.10	0.44	2		212.27	2.25	3
	3	2006	10	16	23.2	3.02	0.04	2	0.06	0.01	2	37.70	0.11	2	37.76	0.12	2		187.89	1.94	3
	4	2006	10	16	23.2	1.40	0.02	2	0.32	0.02	2	20.06	0.16	2	20.38	0.17	2		81.6	0.48	2
	5	2006	10	16	23.2	0.17	0.01	2	0.09	0.01	2	0.33	0.01	2	0.42	0.02	2				9
	6	2006	10	16	23.2	1.42	0.01	2	0.16	0.01	2	10.06	0.07	2	10.22	0.07	2		174.65	1.36	3
51																					
	1	2007	1	16	20.3	0.47		2	0.66		2	6.27		2			9		29.77		2
	2	2007	1	16	20.3	2.58		2	0.13		2	34.24		2			9		153.99		2
	3	2007	1	16	20.3	3.10		2	0.06		2	42.40		2			9		131.46		2
	4	2007	1	16	20.3	1.62		2	0.41		2	20.94		2			9		60.76		2
	5	2007	1	16	20.3	0.01		2	0.04		2	0.14		2			9		1.36		2
	6	2007	1	16	20.3	1.65		2	0.43		2	21.23		2			9		61.06		2
52																					
	1	2006	12	12		0.48	0.00	2	0.60	0.00	2	5.60	0.01	2			9		31.8	0.1	2
	2	2006	12	12		2.43	0.01	2	0.08	0.00	2	33.0	0.1	2			9		168	0	2
	3	2006	12	12		2.92	0.00	2	0.00	0.00	2	41.6	0.0	2			9		146	0	2
	4	2006	12	12		1.55	0.00	2	0.33	0.00	2	21.3	0.0	2			9		63.2	0.2	2
	5	2006	12	12		0.03	0.00	2	0.00	0.01	2	0.00	0.01	2			9		1.64	0.03	2
	6	2006	12	12		1.55	0.01	2	0.33	0.00	2	21.3	0.0	2			9		63.0	0.1	2
53																					
	1	2006	8	31		0.45		2	0.61		2	5.47		2	6.08		2		32.11		2
	2	2006	8	31		2.42		2	0.10		2	34.14		2	34.24		2		158.36		2
	3	2006	8	31		2.92		2	0.01		2	42.90		2	42.91		2		136.87		2
	4	2006	8	31		1.56		2	0.34		2	21.27		2	21.61		2		56.62		2
	5	2006	8	31		0.05		2	0.02		2	0.13		2	0.15		2		2.64		2
	6	2006	8	31		1.53		2	0.35		2	21.13		2	21.48		2		58.18		2
54																					
	1	2006	12	18		0.46		2	0.63		2	5.15		2	5.78		2		29.43		2
	2	2006	12	18		2.49		2	0.10		2	33.58		2	33.68		2		157.73		2
	3	2006	12	18		3.01		2	0.01		2	43.42		2	43.43		2		137.28		2
	4	2006	12	18		1.60		2	0.34		2	21.06		2	21.40		2		59.41		2
	5	2006	12	18		0.01		2	0.02		2	0.01		2	0.03		2		1.22		2
	6	2006	12	18		1.60		2	0.35		2	21.02		2	21.37		2		59.26		2

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Table A3. (Continued)

2006 RMNS Intercomparison Exercise

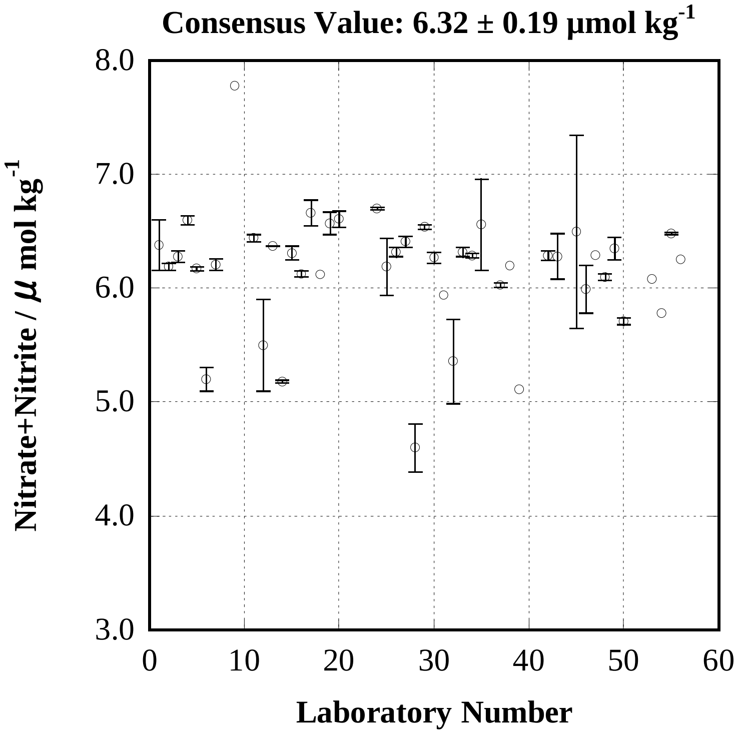
LAB	SAMPLE	YEAR	MON	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
55																					
	1	2006	10	5	24.8	0.47	0.00	6	0.62	0.00	6	5.86	0.01	6	6.48	0.01	6	99.9	30.94	0.06	6
	2	2006	10	5	24.8	2.51	0.00	6	0.09	0.00	6	34.18	0.07	6	34.26	0.07	6	99.9	158.25	0.26	6
	3	2006	10	5	24.8	3.01	0.00	6	0.00	0.00	6	42.92	0.05	6	42.92	0.05	6	99.9	138.11	0.19	6
	4	2006	10	5	24.8	1.59	0.00	6	0.34	0.00	6	22.16	0.03	6	22.50	0.03	6	99.9	60.99	0.05	6
	5	2006	10	5	24.8	0.02	0.00	6	0.01	0.00	6	0.03	0.01	6	0.03	0.01	6	99.9	1.86	0.05	6
	6	2006	10	5	24.8	1.60	0.00	6	0.34	0.00	6	22.19	0.02	6	22.53	0.02	6	99.9	61.03	0.09	6
56																					
	1					0.5		2			9			9	6.40		2		29.67		2
	2					2.51		2			9			9	33.80		2		155.92		2
	3					3.03		2			9			9	40.81		2		135.79		2
	4					1.6		2			9			9	21.77		2		58.87		2
	5					0.05		2			9			9	0.01		2		1.7		2
	6					1.55		2			9			9	22.0		2		58.57		2

Flag: 2: acceptable measurement, 3: questionable, 4: bad, 5: below detction limit, 6: mean of replicate measurement, 9: not reported

Appendix III

Scatter plots and histograms of the results

Sample 1　Nitrate+Nitrite



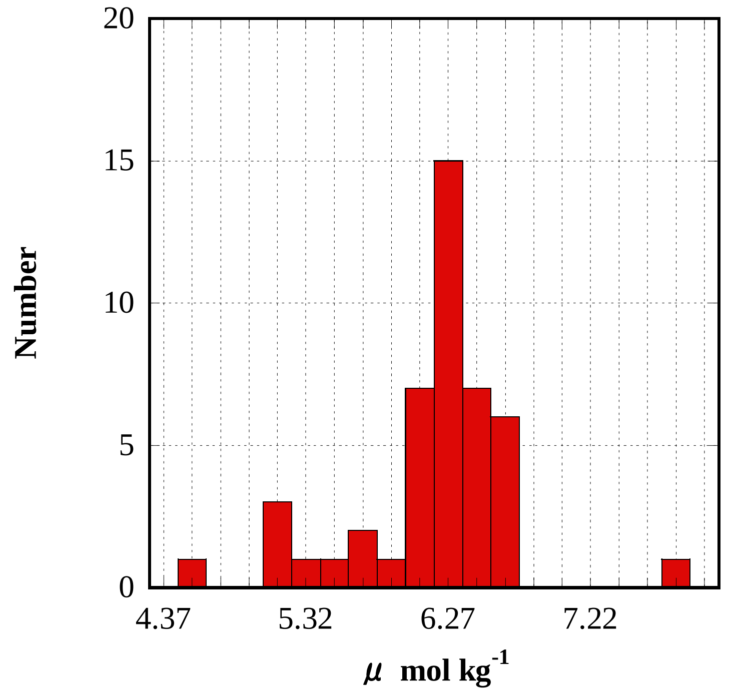


Figure A1-1 Nitrate+nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate+nitrite concentration of sample #1 (lower panel)

Sample 2 Nitrate+Nitrite

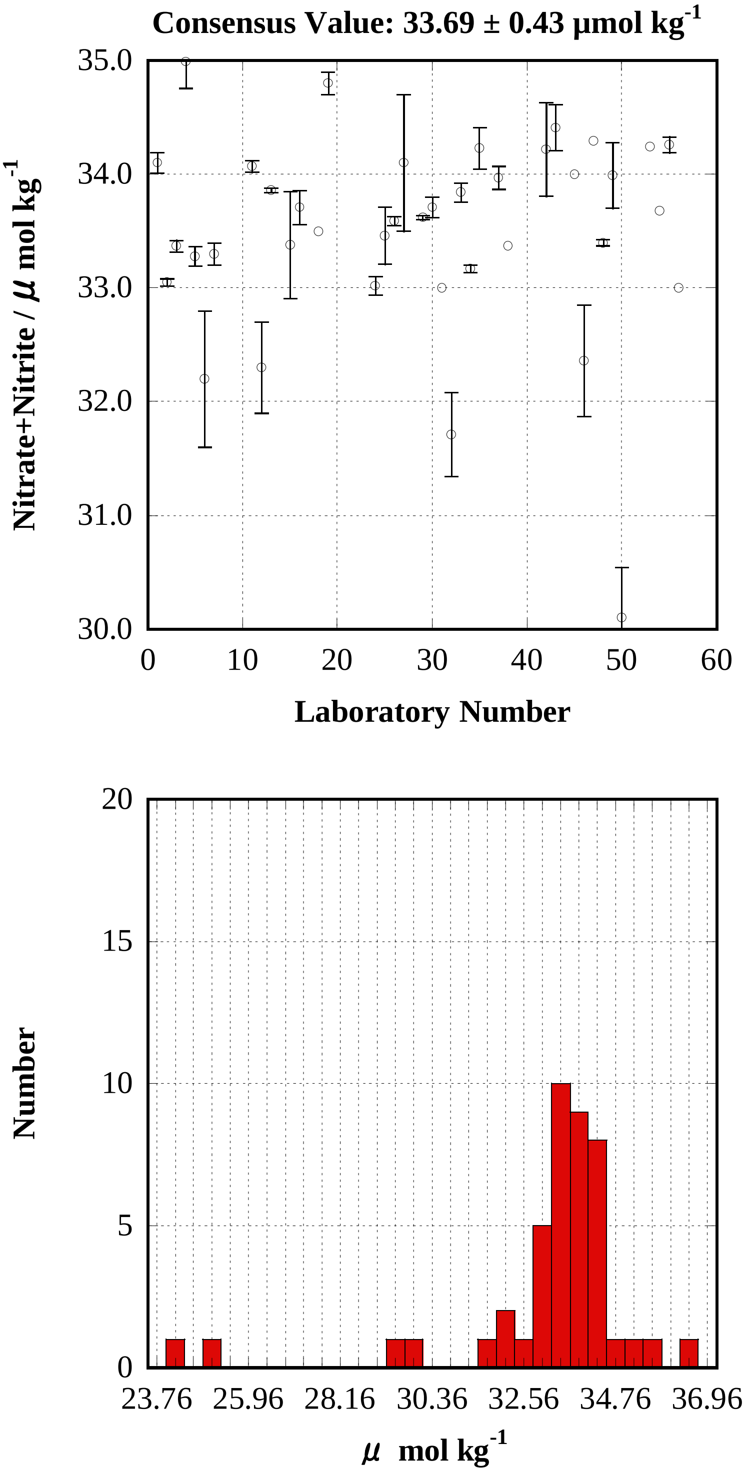


Figure A1-2 Nitrate+nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate+nitrite concentration of sample #2 (lower panel)

Sample 3 Nitrate+Nitrite

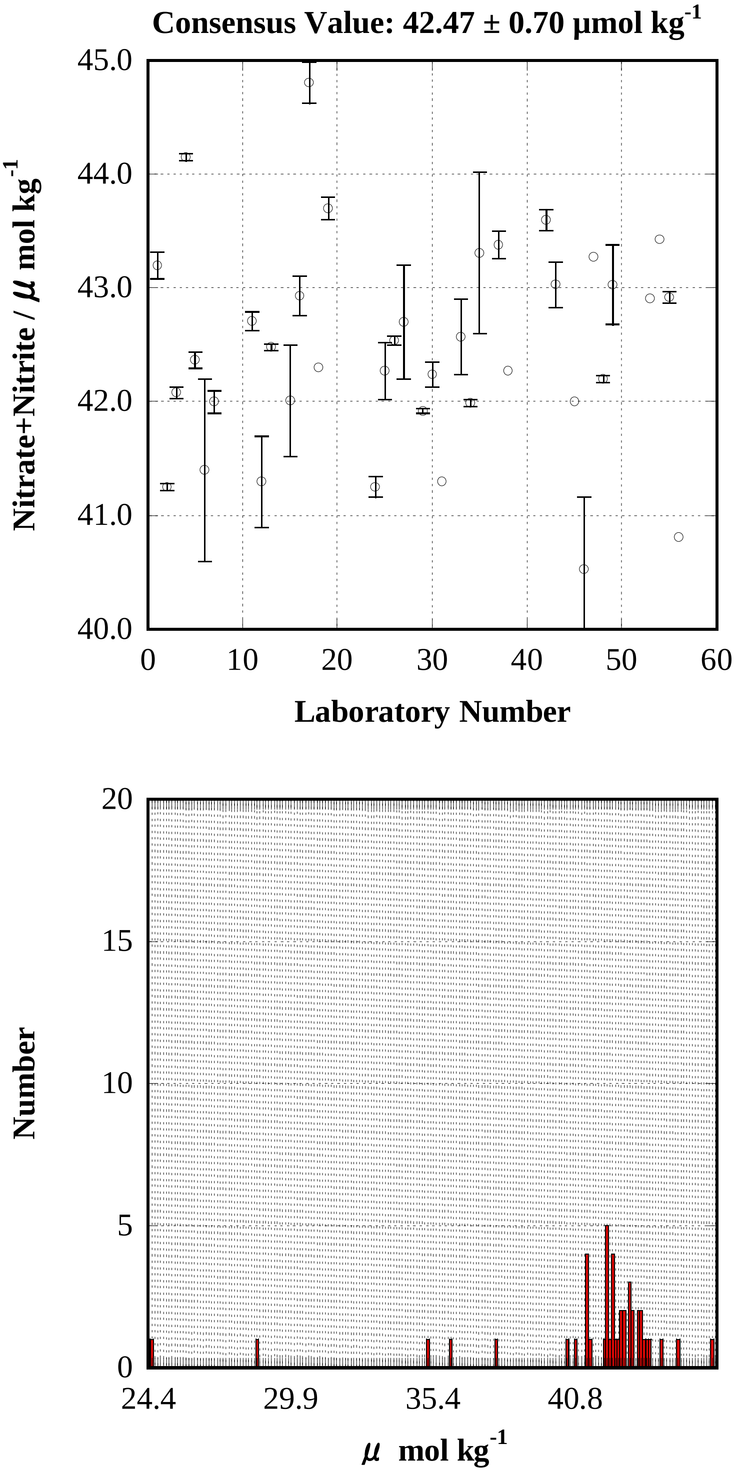
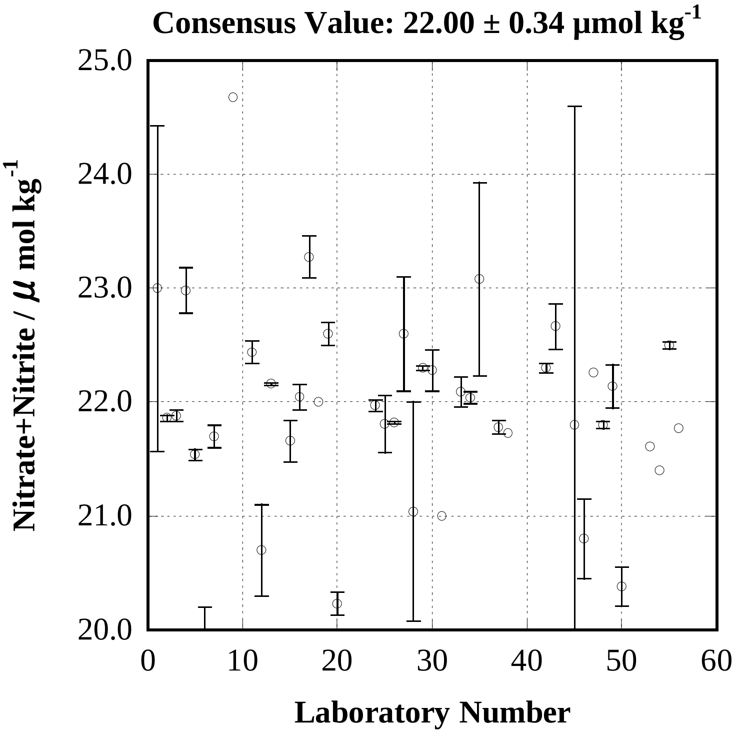


Figure A1-3 Nitrate+nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate+nitrite concentration of sample #3 (lower panel)

Sample 4 Nitrate+Nitrite



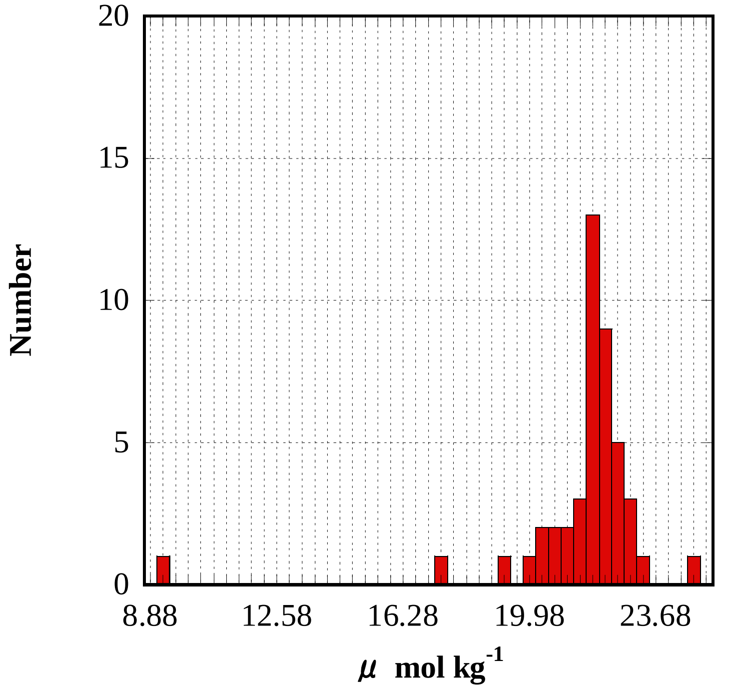


Figure A1-4 Nitrate+nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate+nitrite concentration of sample #4 (lower panel)

Sample 5　Nitrate+Nitrite

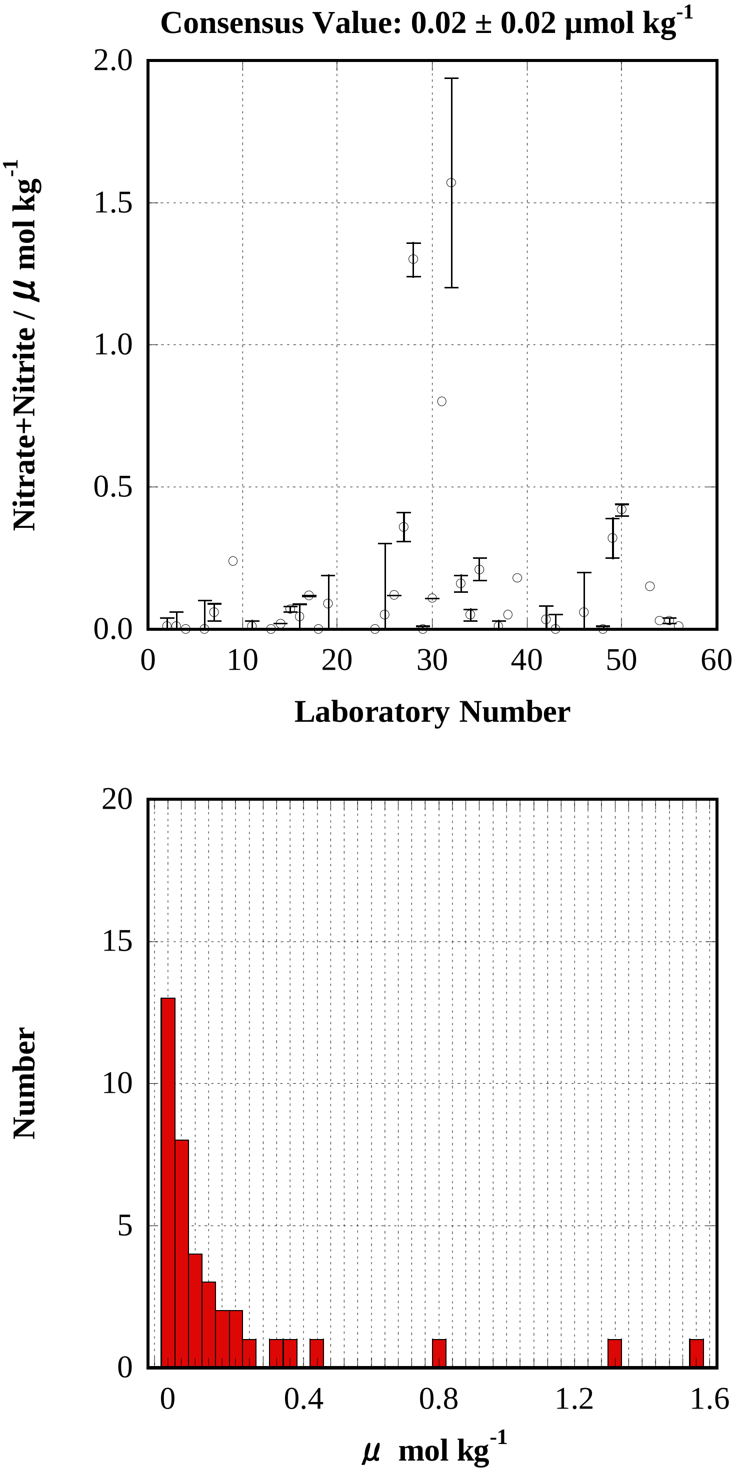
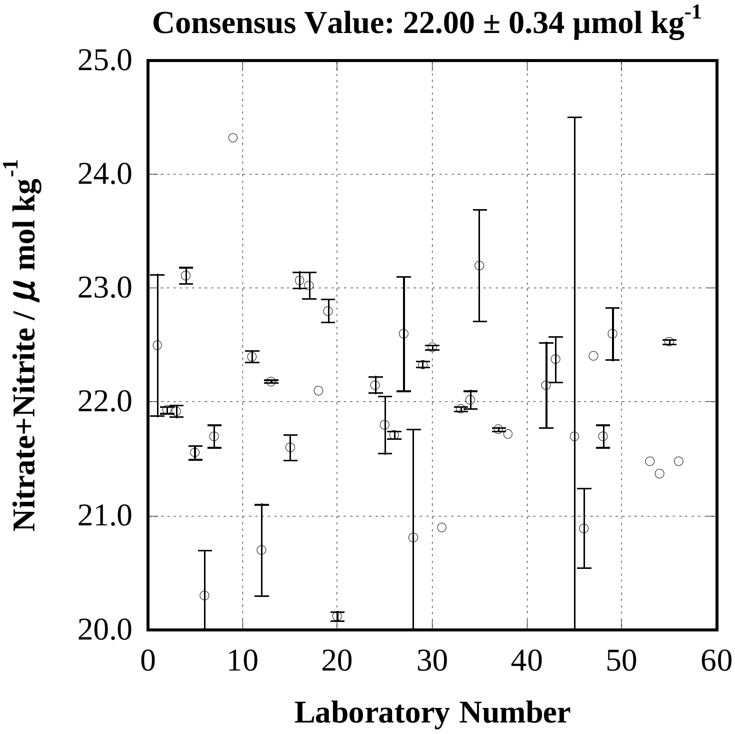


Figure A1-5 Nitrate+nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate+nitrite concentration of sample #5 (lower panel)

Sample 6 Nitrate+Nitrite



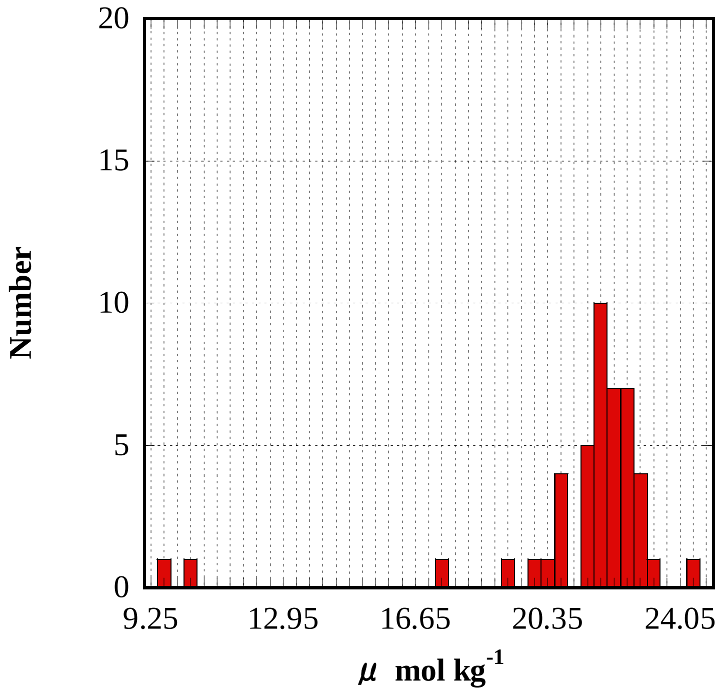
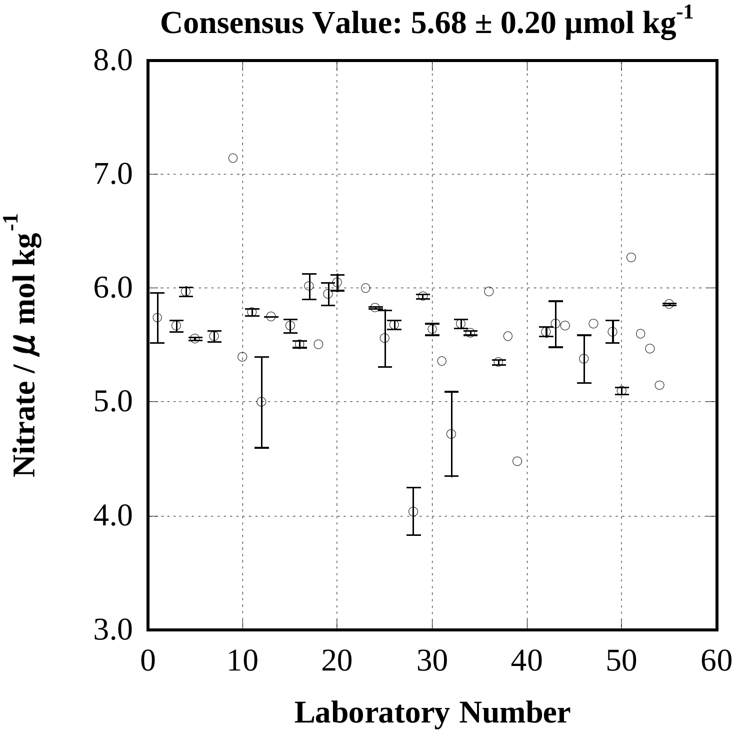


Figure A1-6 Nitrate+nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate+nitrite concentration of sample #6 (lower panel)

Sample 1　Nitrate



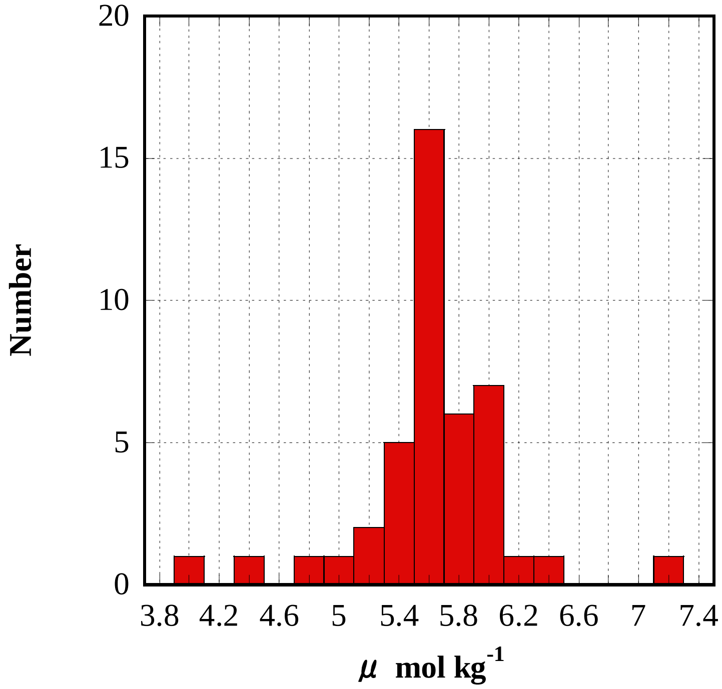


Figure A2-1 Nitrate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate concentration of sample #1 (lower panel)

Sample 2　Nitrate

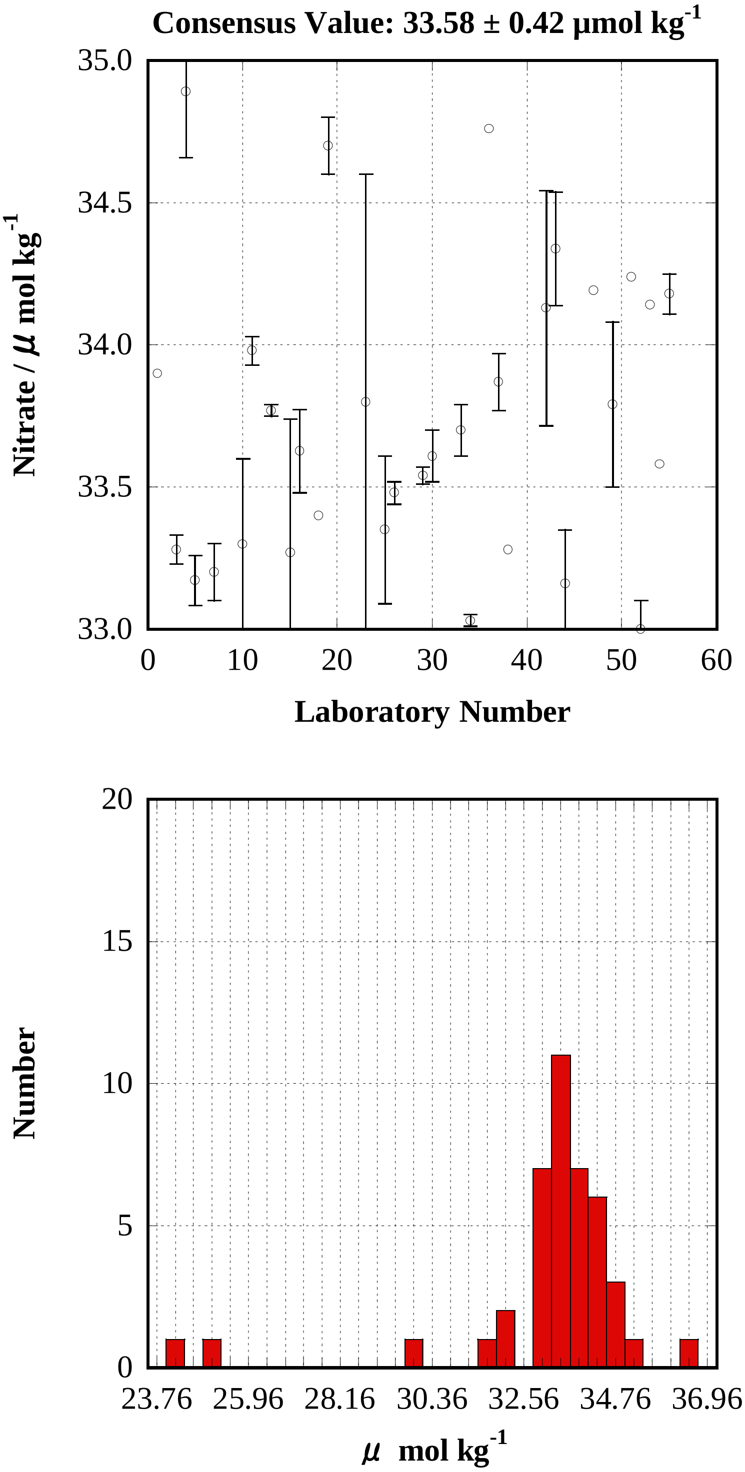
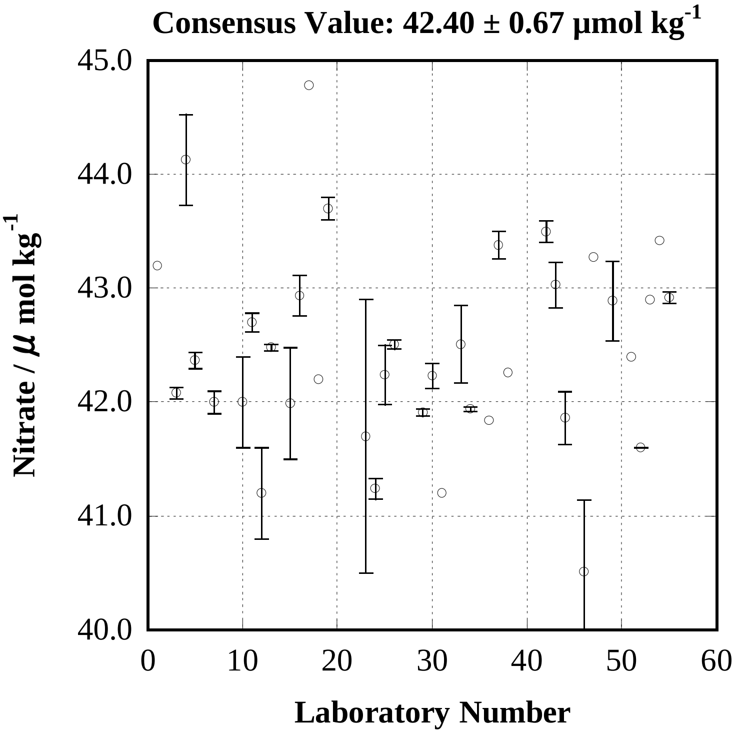


Figure A2-2 Nitrate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate concentration of sample #2 (lower panel)

Sample 3　Nitrate



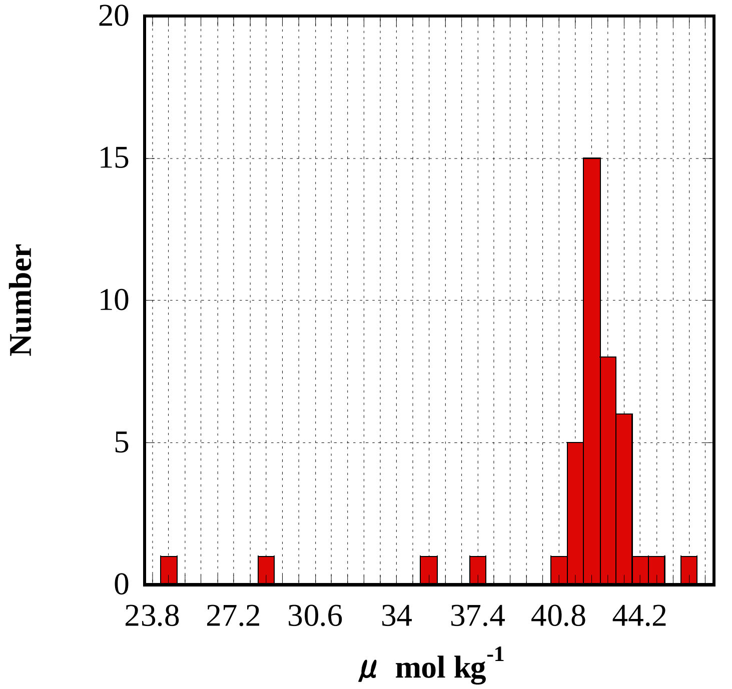


Figure A2-3 Nitrate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate concentration of sample #3 (lower panel)

Sample 4　Nitrate

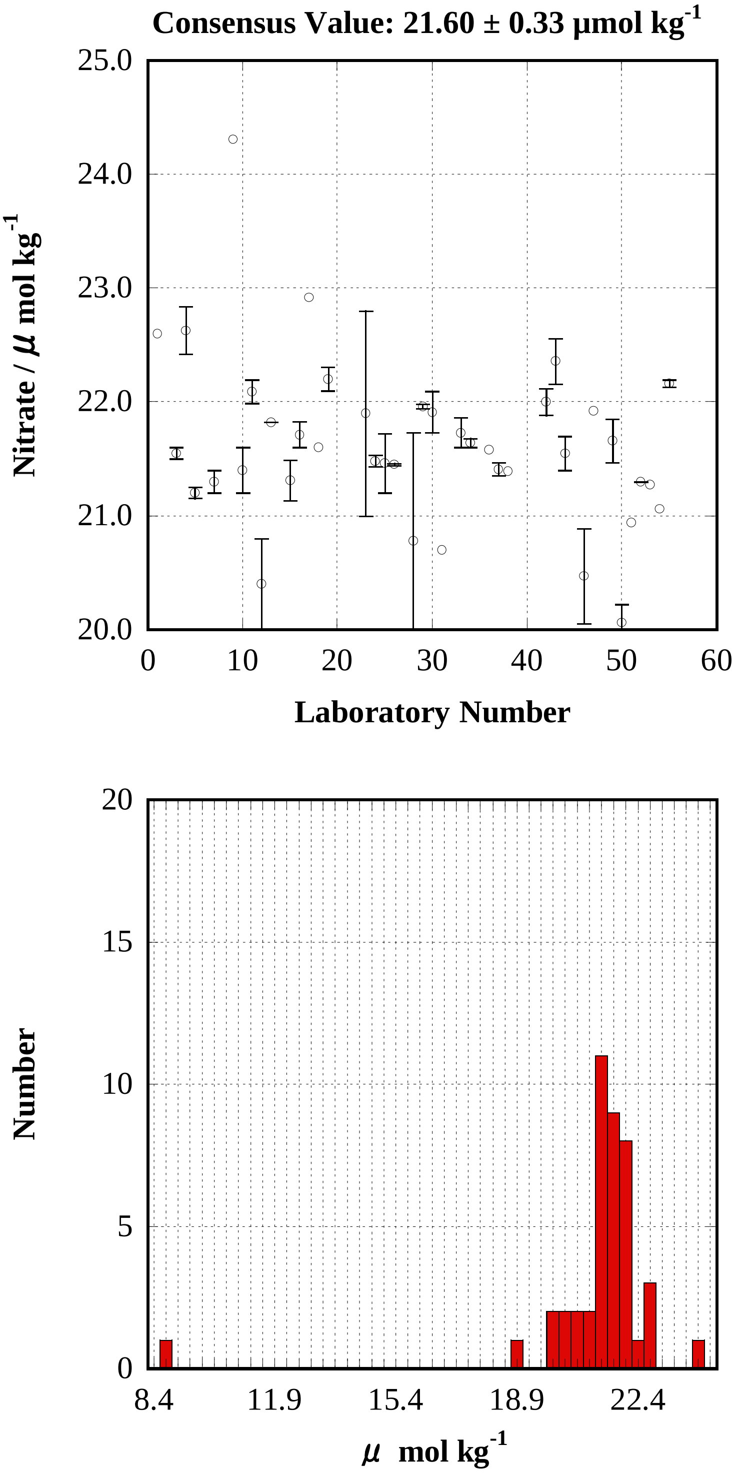


Figure A2-4 Nitrate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate concentration of sample #4 (lower panel)

Sample 5　Nitrate

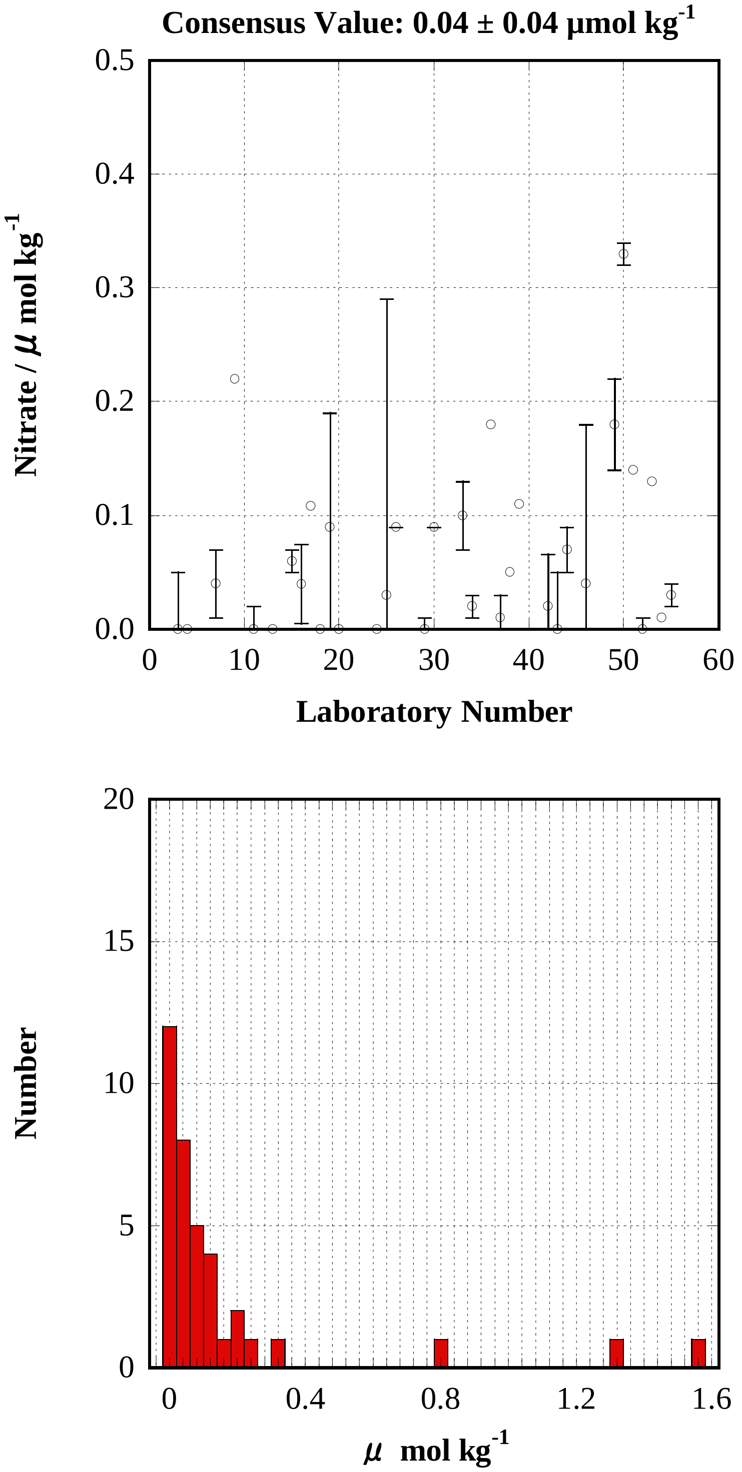


Figure A2-5 Nitrate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate concentration of sample #5 (lower panel)

Sample 6 Nitrate

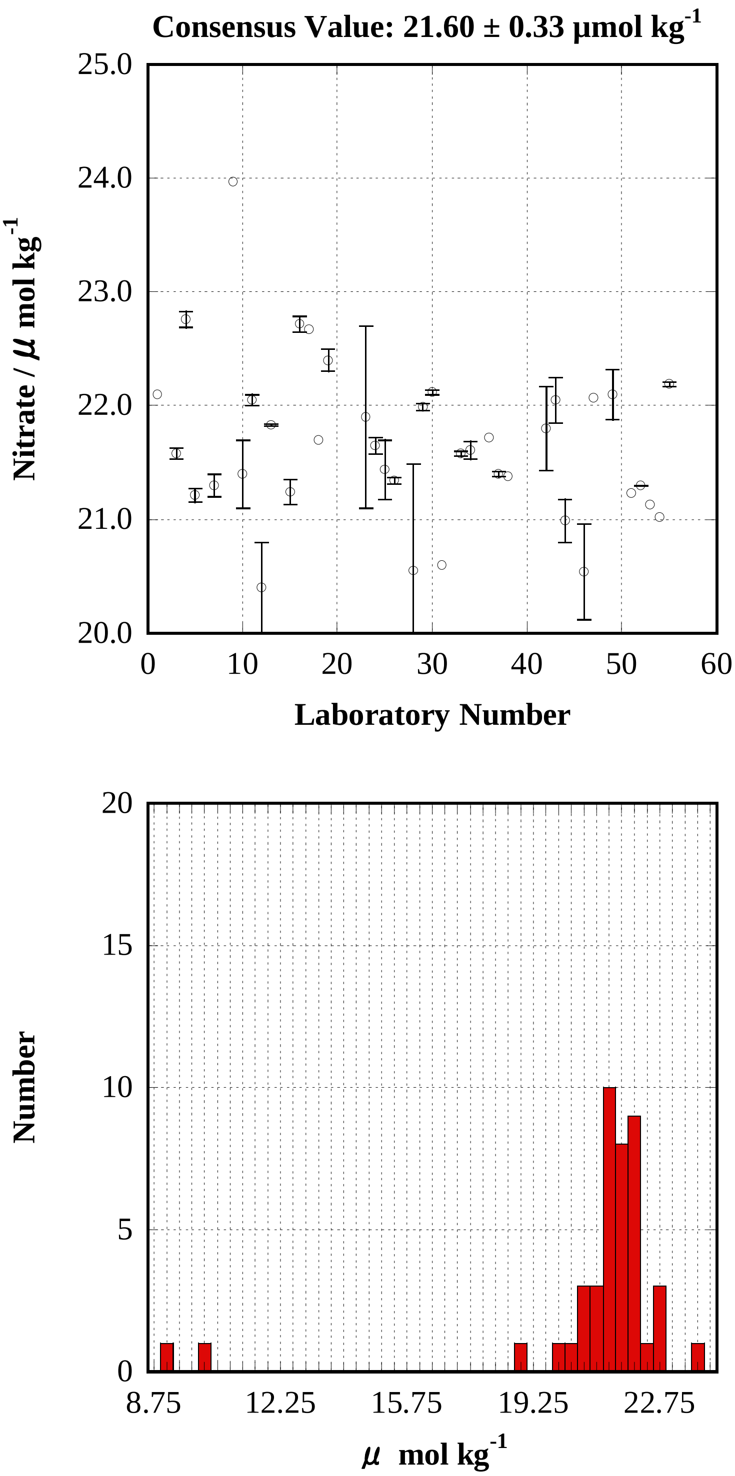


Figure A2-6 Nitrate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrate concentration of sample #6 (lower panel)

Sample 1　Nitrite

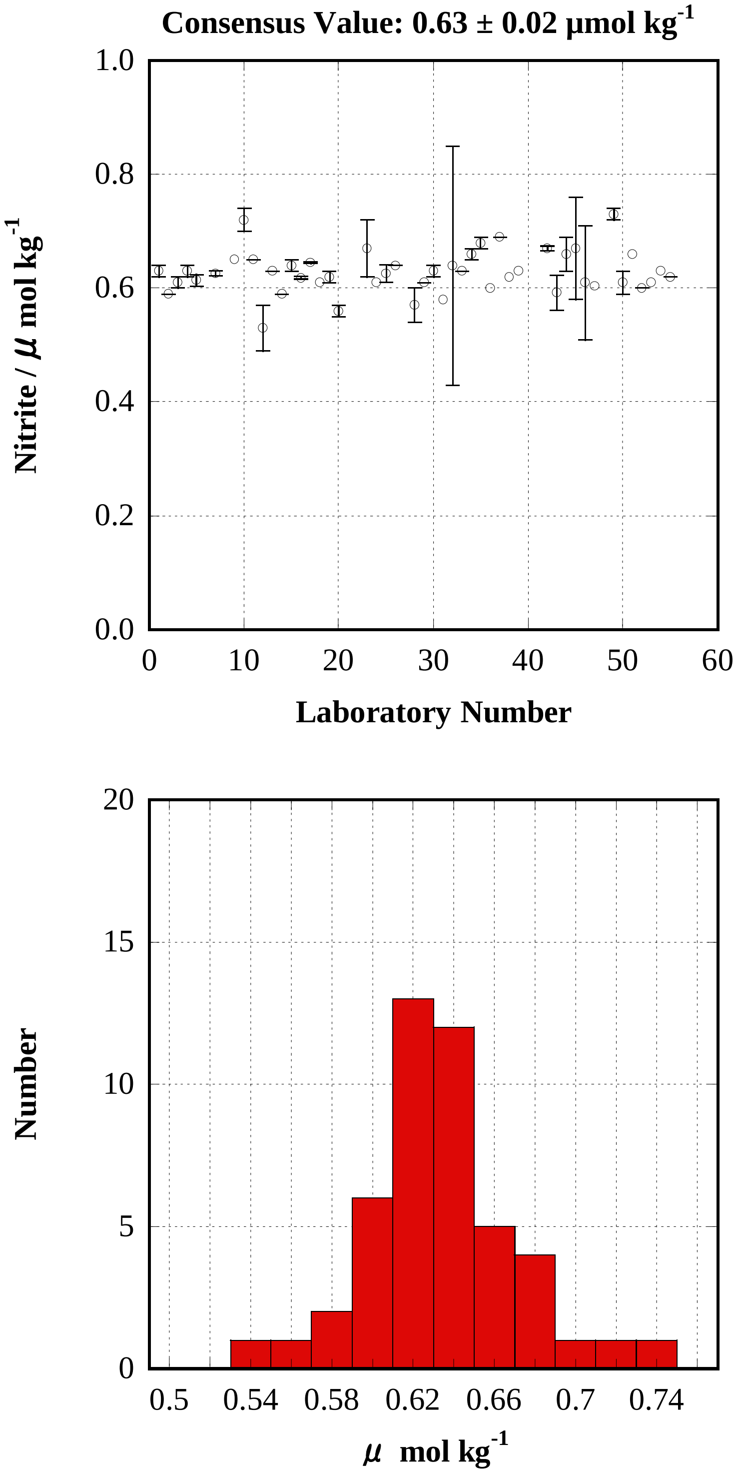
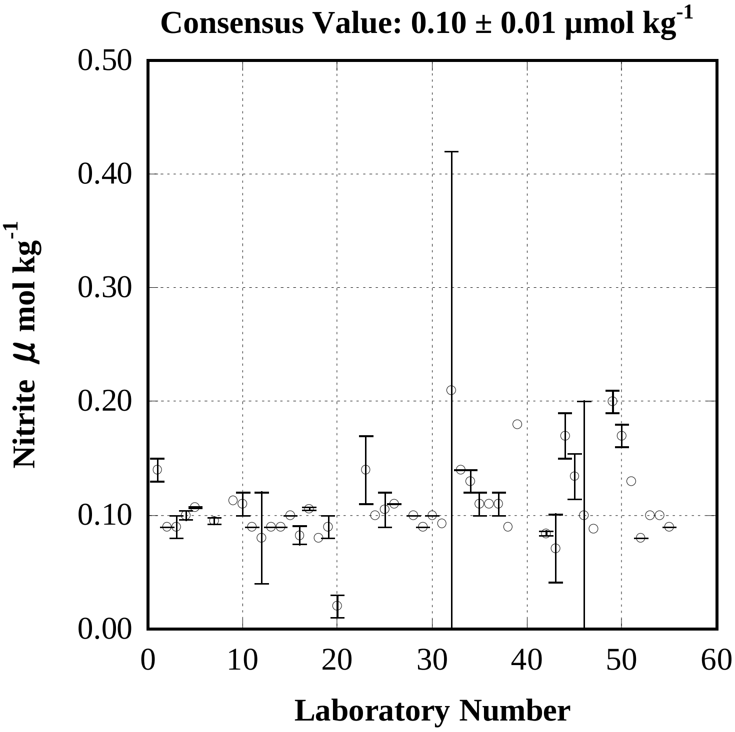


Figure A3-1 Nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrite concentration of sample #1 (lower panel)

Sample 2　Nitrite



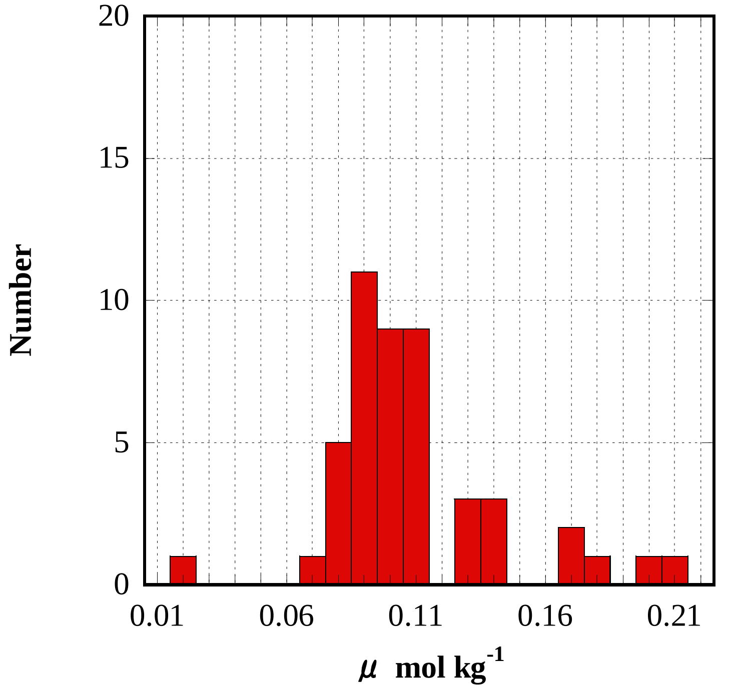


Figure A3-2 Nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrite concentration of sample #2 (lower panel)

Sample 3 Nitrite

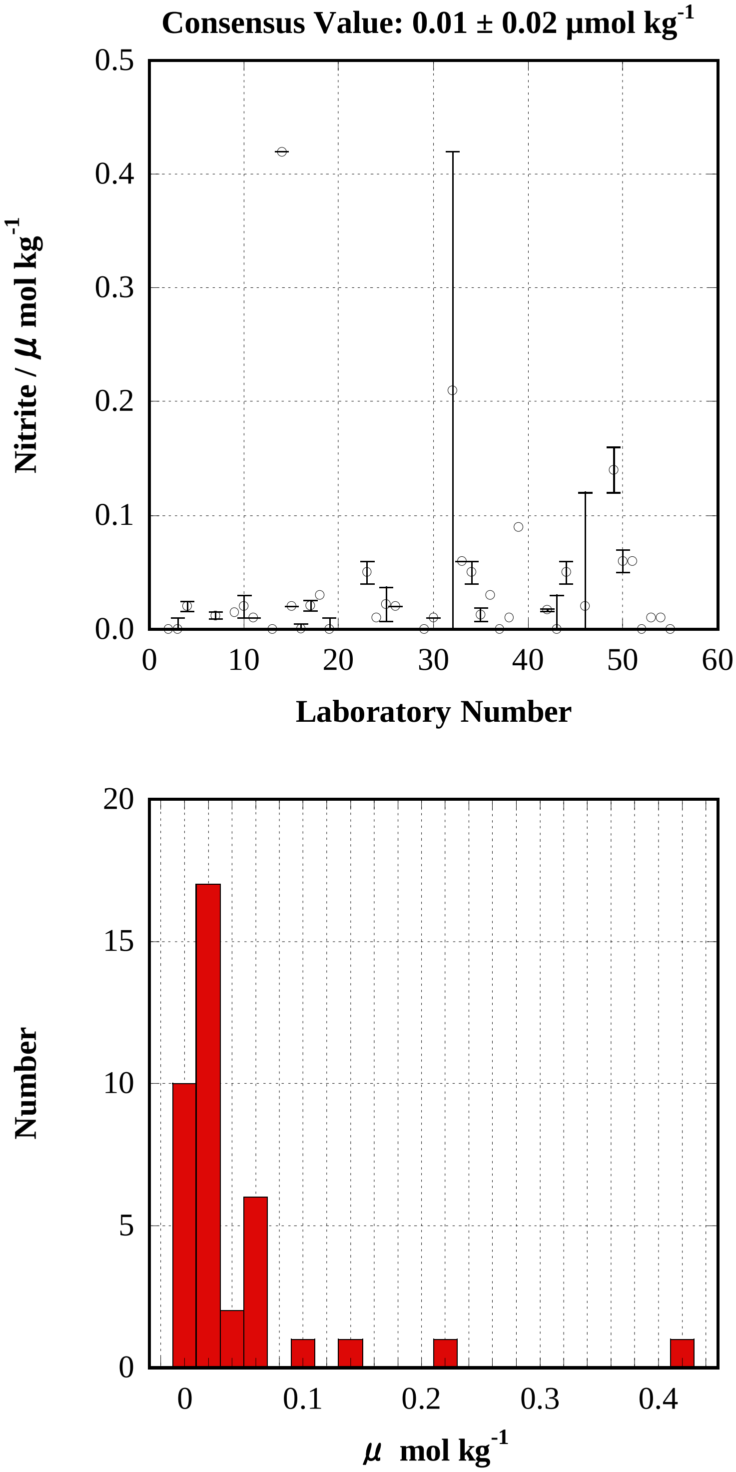
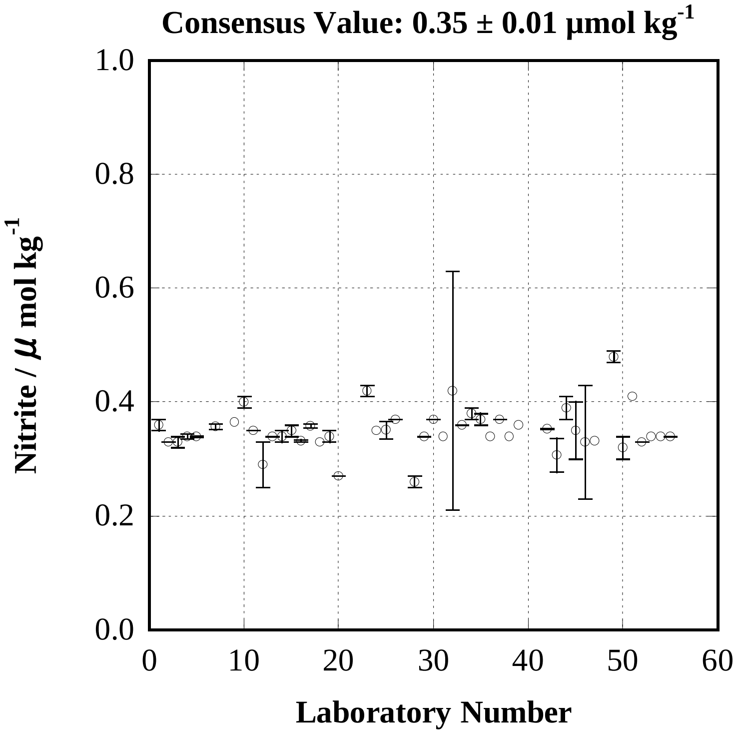


Figure A3-3 Nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrite concentration of sample #3 (lower panel)

Sample 4 Nitrite



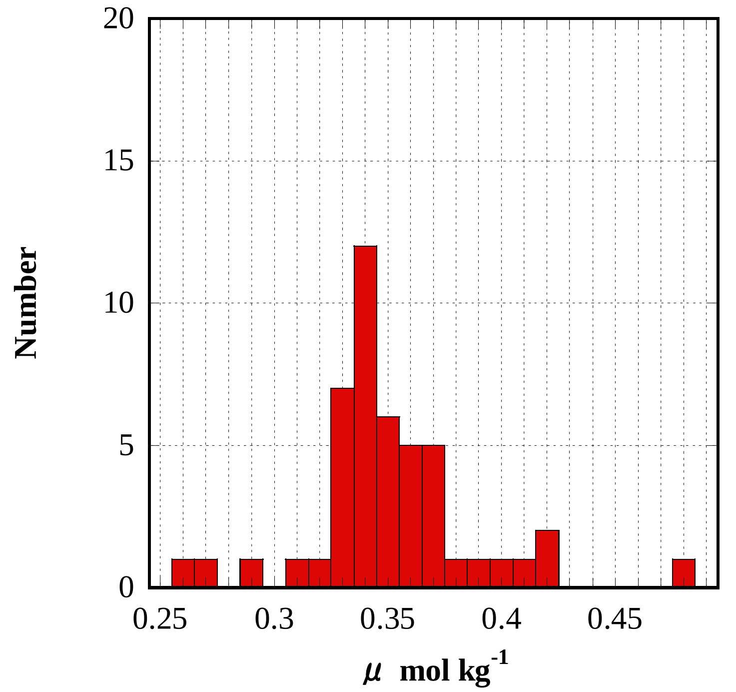


Figure A3-4 Nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrite concentration of sample #4 (lower panel)

Sample 5　Nitrite

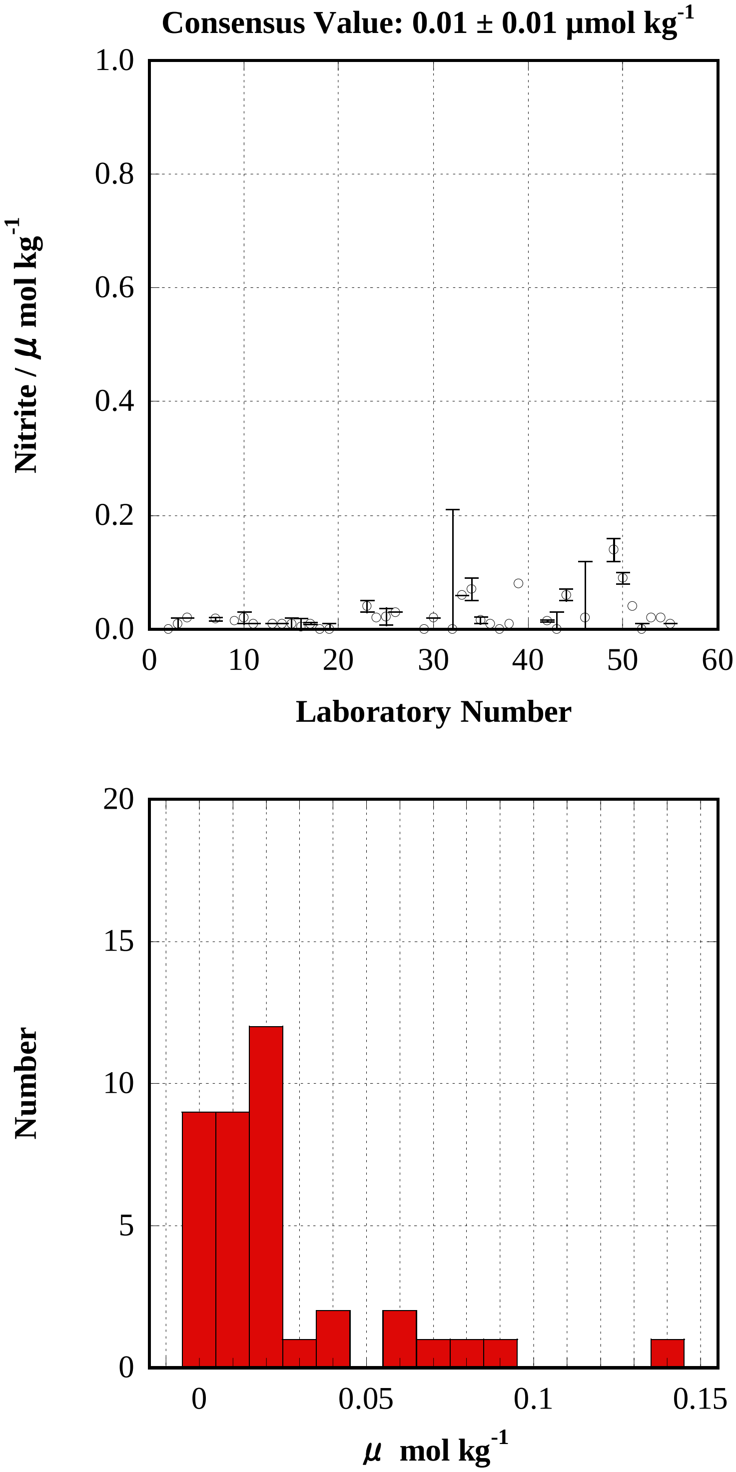


Figure A3-5 Nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrite concentration of sample #5 (lower panel)

Sample 6 Nitrite

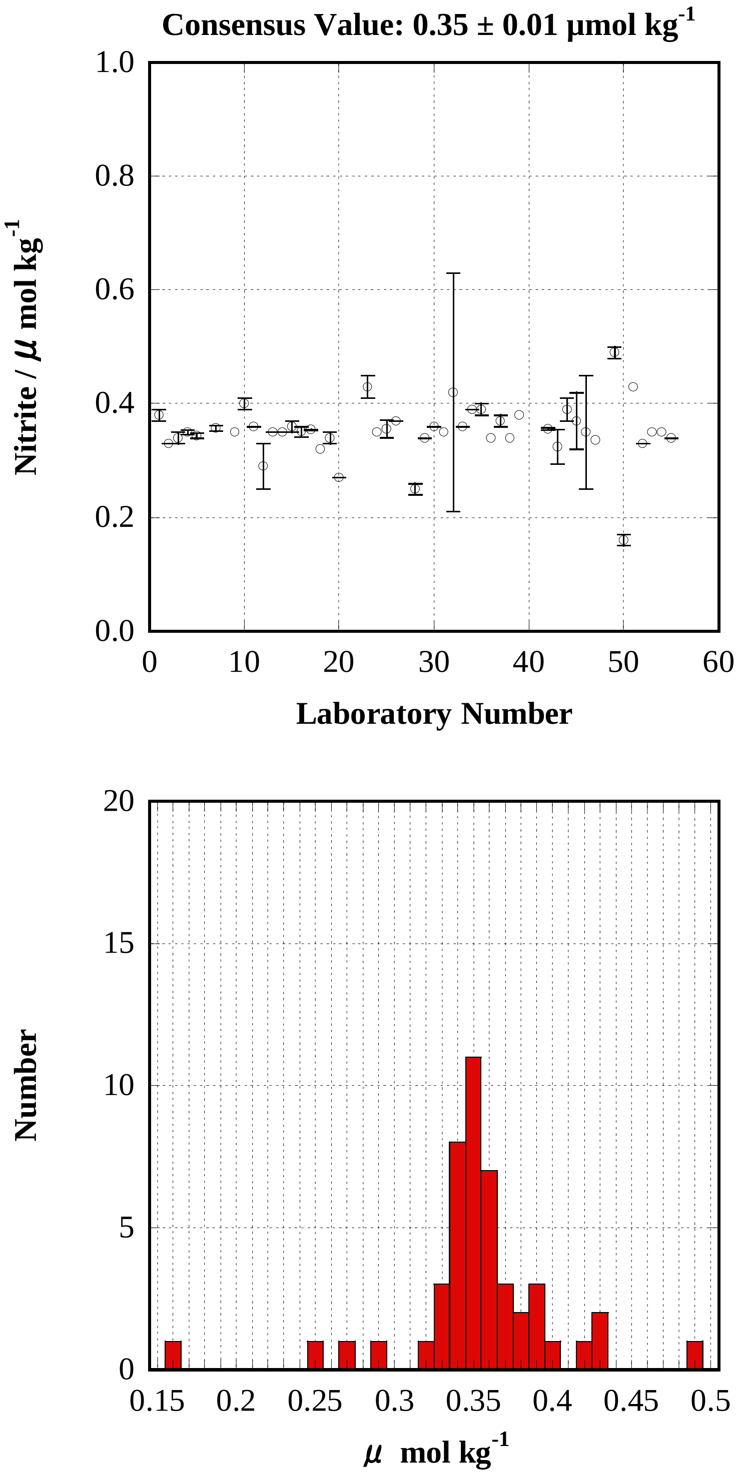
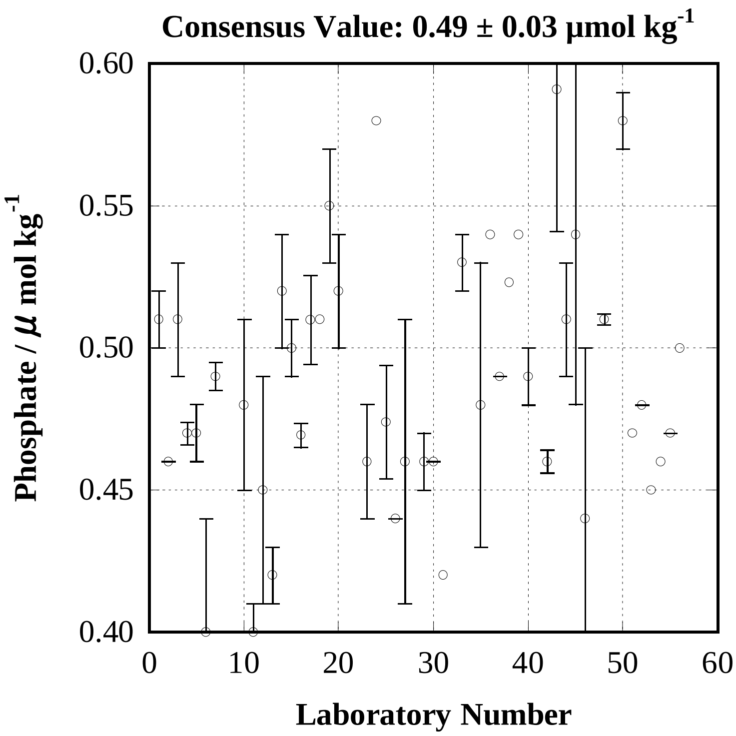


Figure A3-6 Nitrite results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of nitrite concentration of sample #6 (lower panel)

Sample 1 Phosphate



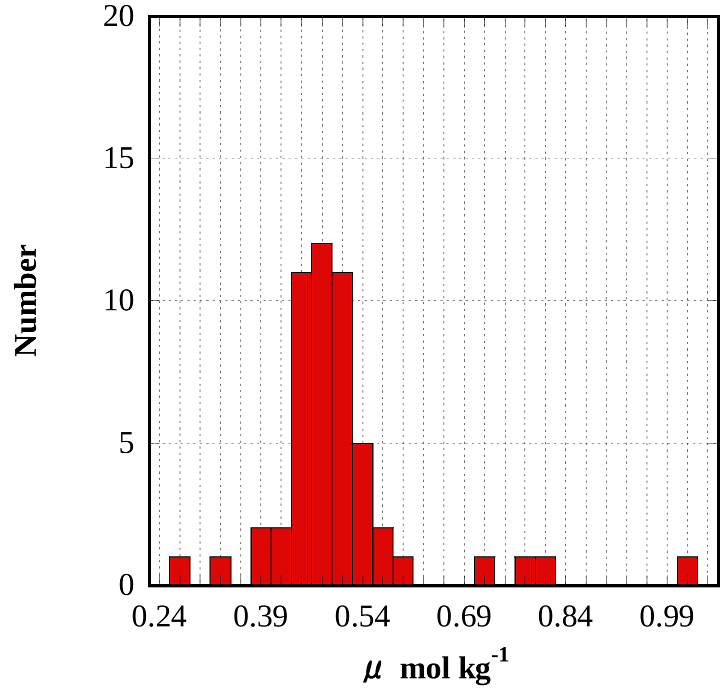
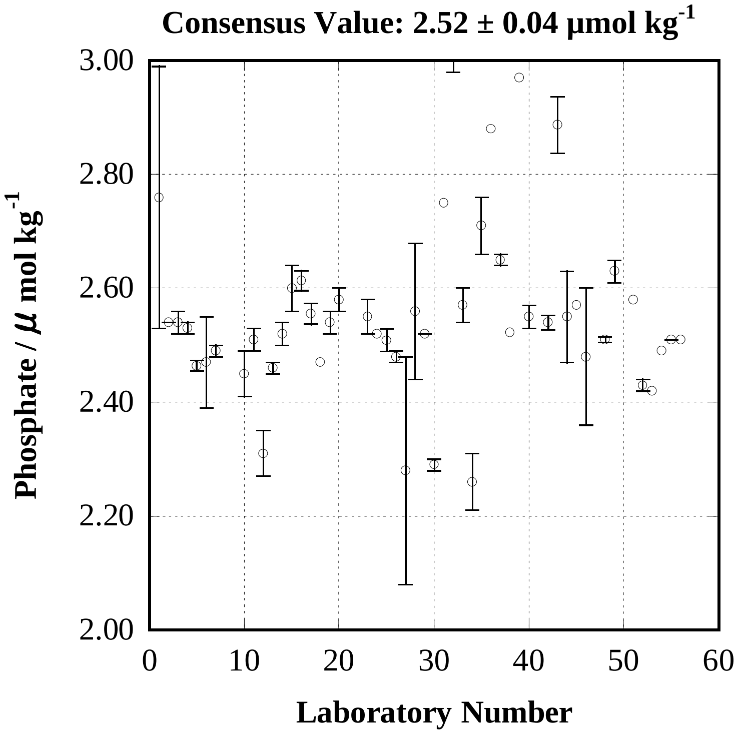


Figure A4-1 Phosphate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of phosphate concentration of sample #1 (lower panel)

Sample 2　Phosphate



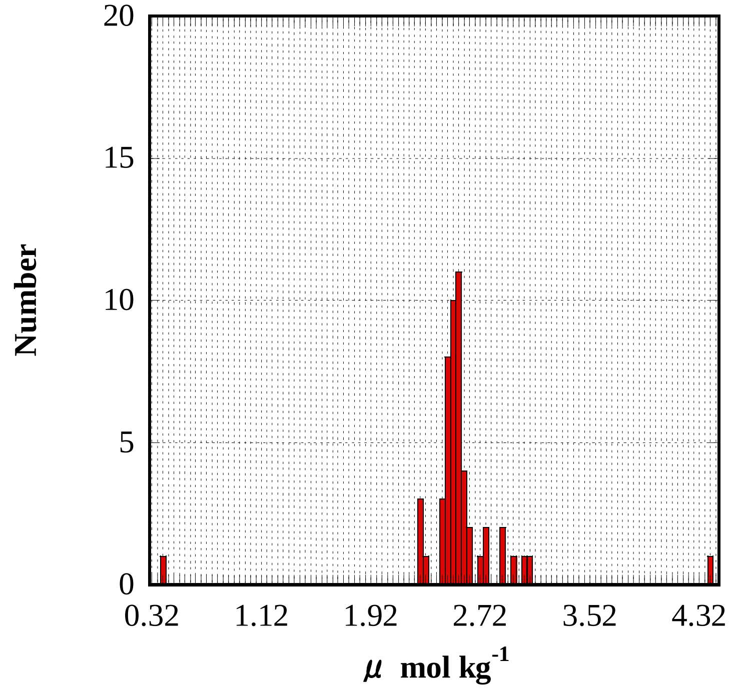
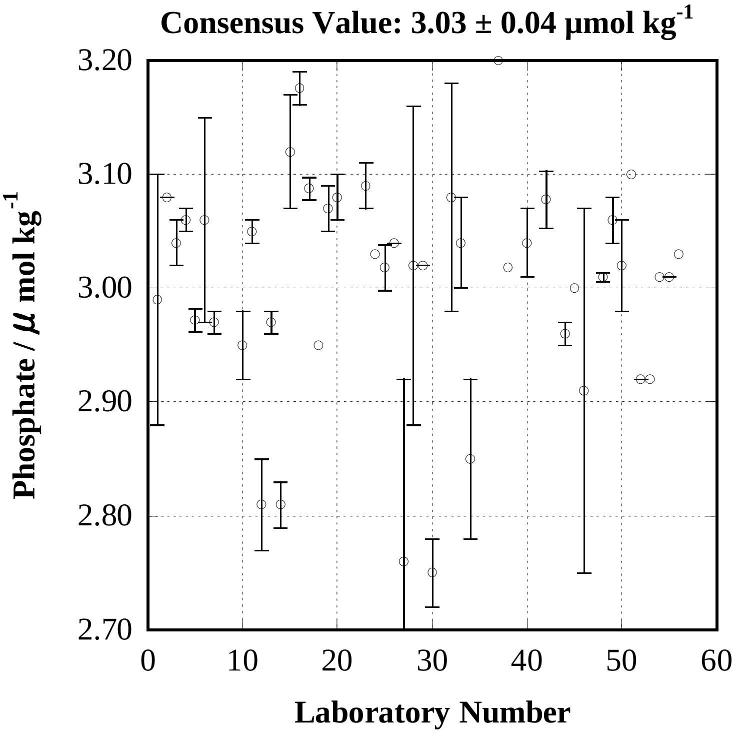


Figure A4-2 Phosphate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of phosphate concentration of sample #2 (lower panel)

Sample 3 Phosphate



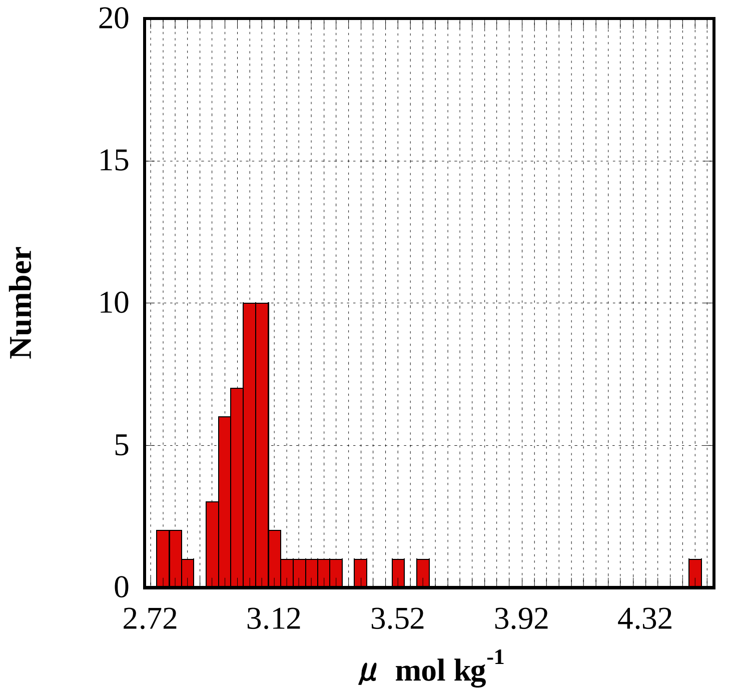
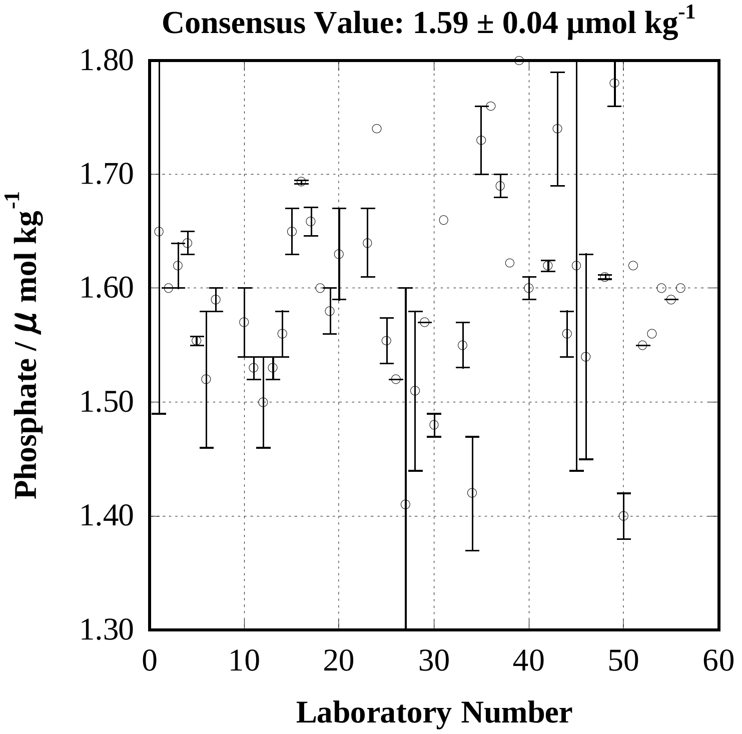


Figure A4-3 Phosphate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of phosphate concentration of sample #3 (lower panel)

Sample 4 Phosphate



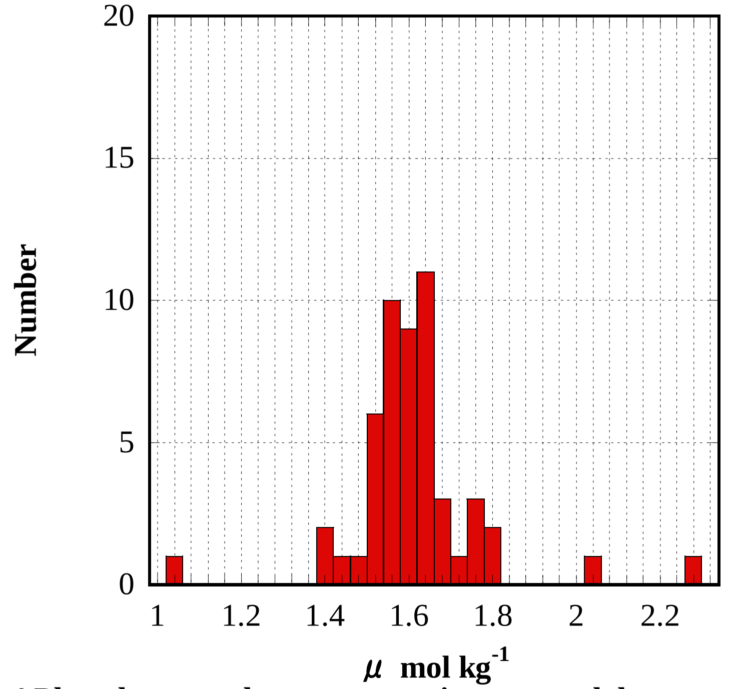


Figure A4-4 Phosphate results: concentrations *versus* **laboratory number (upper panel)**
Frequency distribution of phosphate concentration of sample #4 (lower panel)

Sample 5 Phosphate

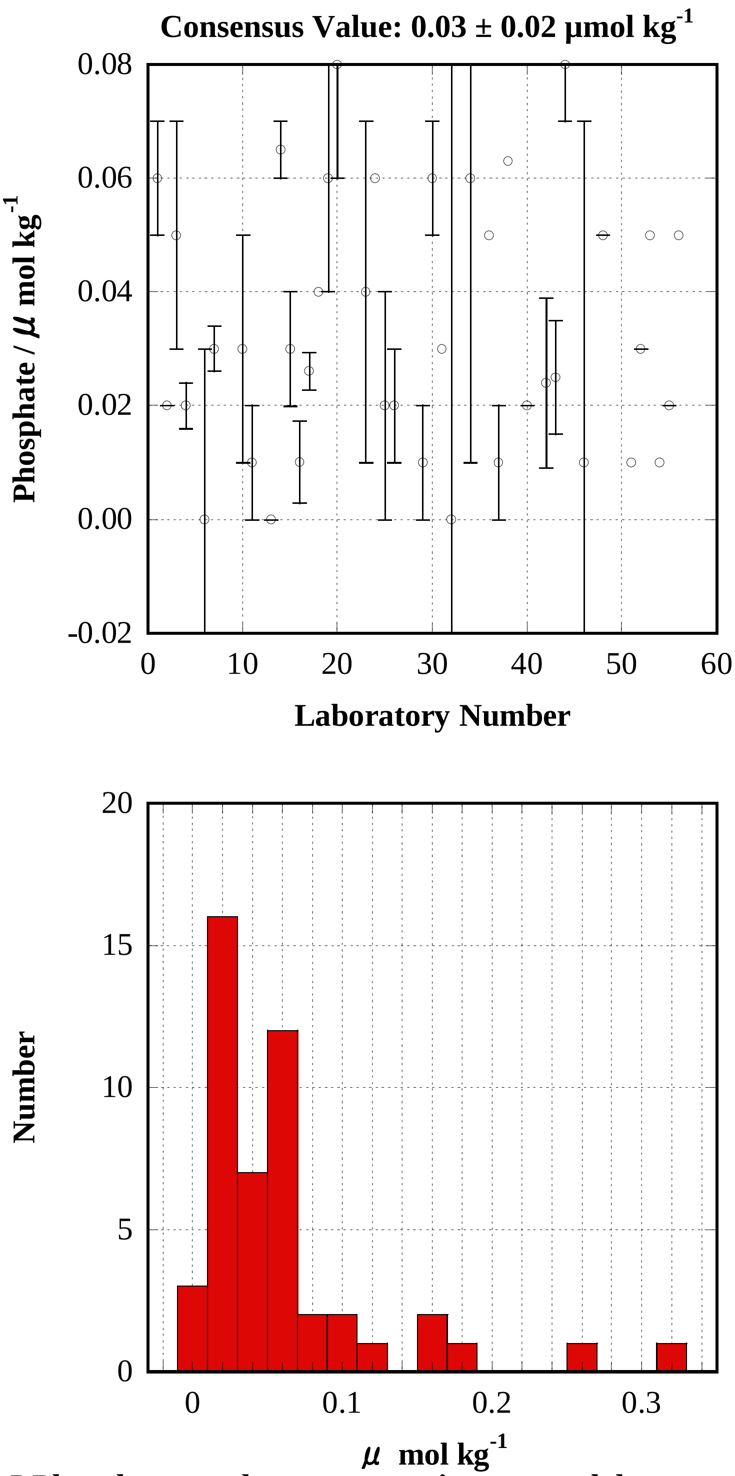


Figure A4-5 Phosphate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of phosphate concentration of sample #5 (lower panel)

Sample 6 Phosphate

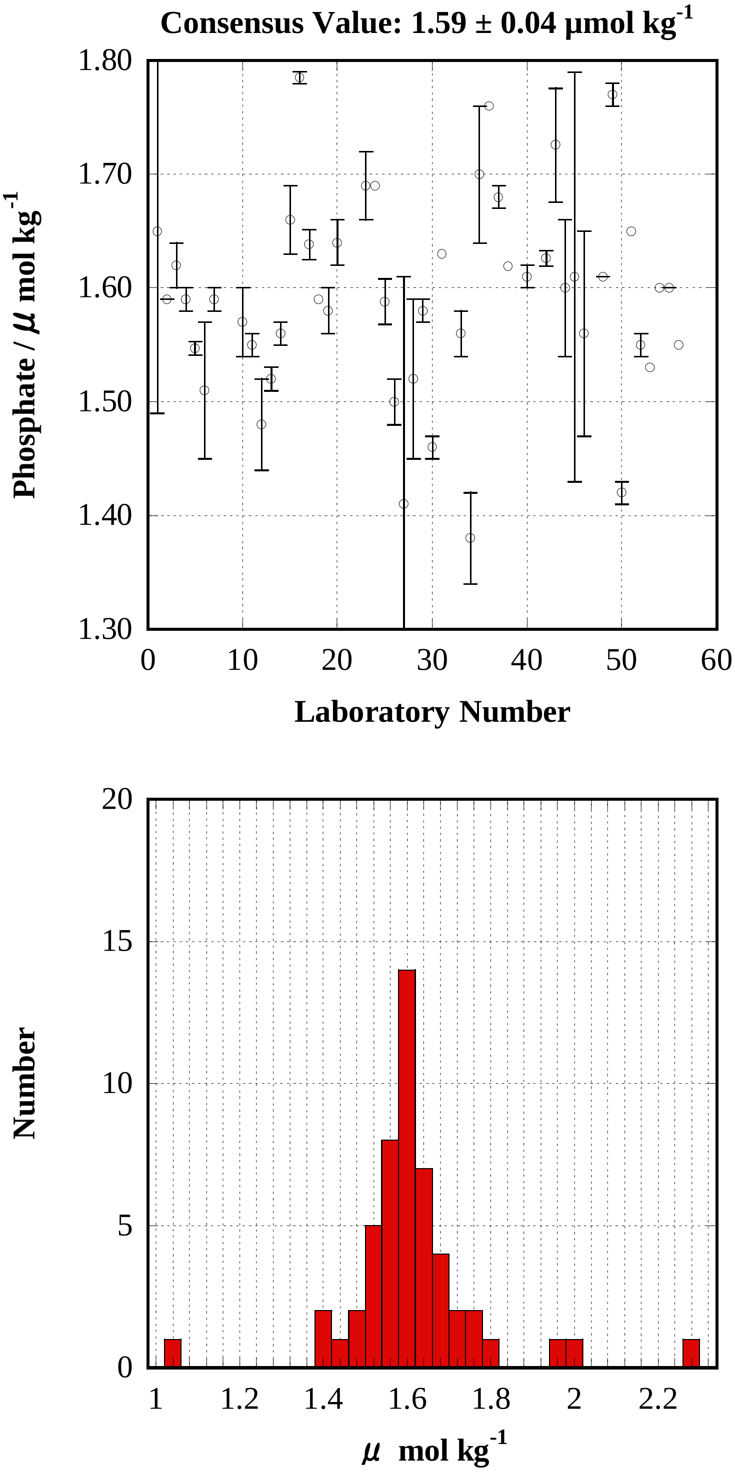
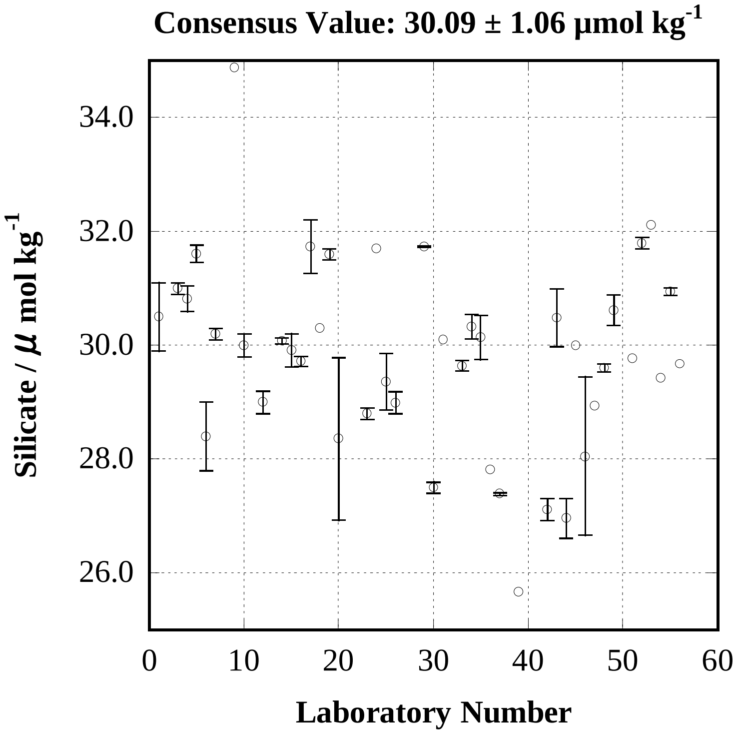


Figure A4-6 Phosphate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of phosphate concentration of sample #6 (lower panel)

Sample 1　Silicate



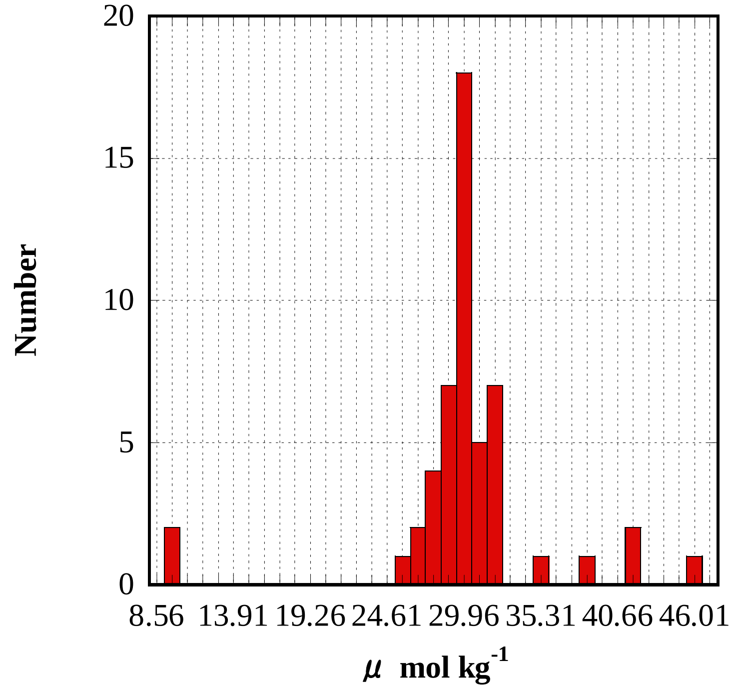


Figure A5-1 Silicate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of silicate concentration of sample #1 (lower panel)

Sample 2 Silicate

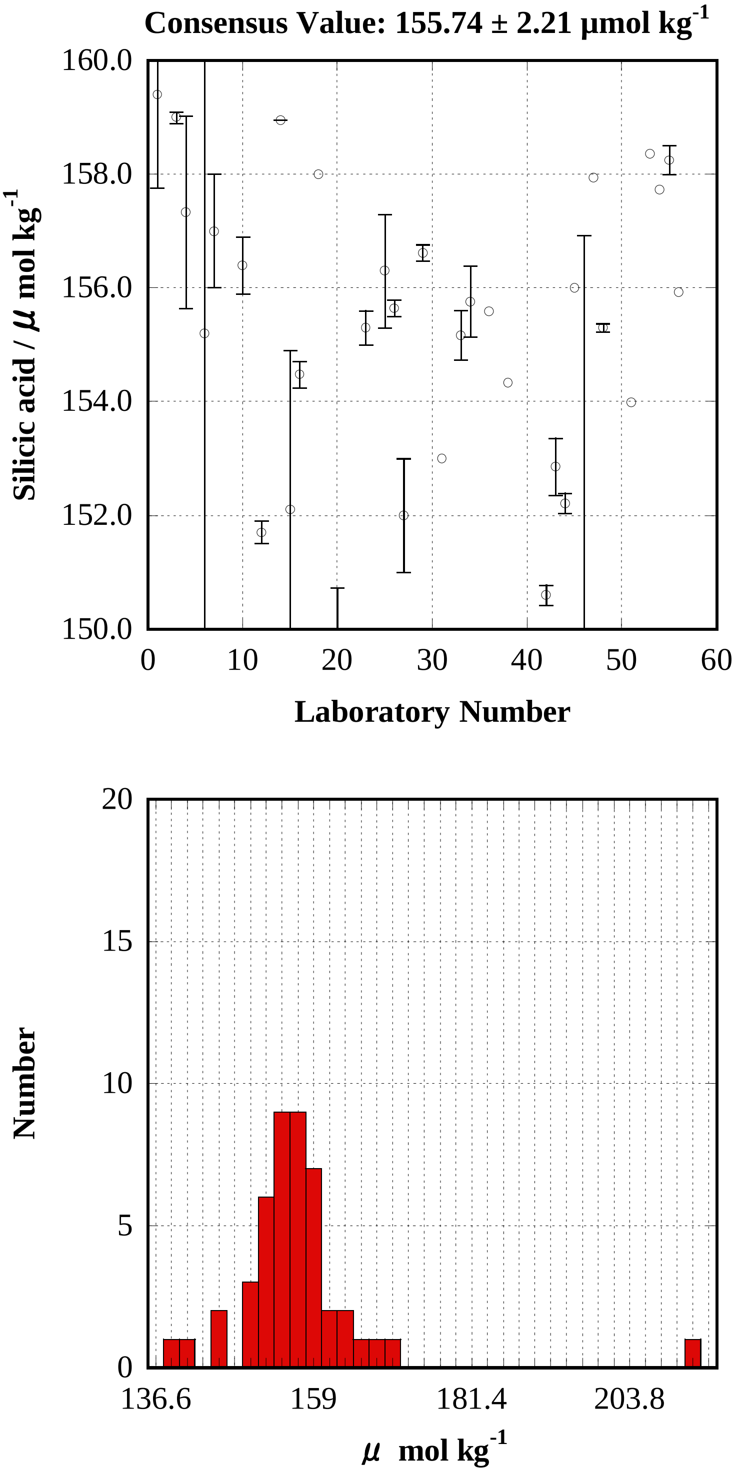
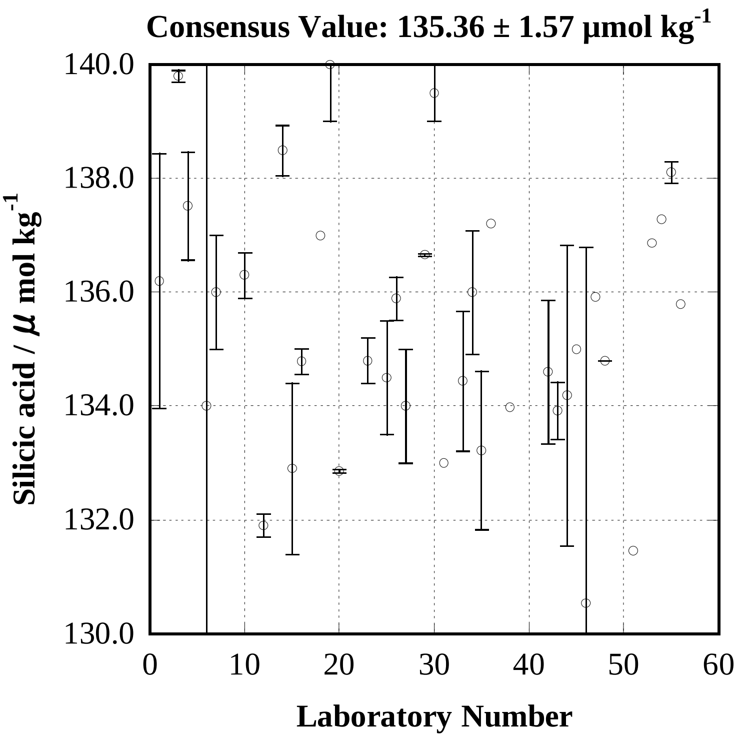


Figure A5-2 Silicate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of silicate concentration of sample #2 (lower panel)

Sample 3　Silicate



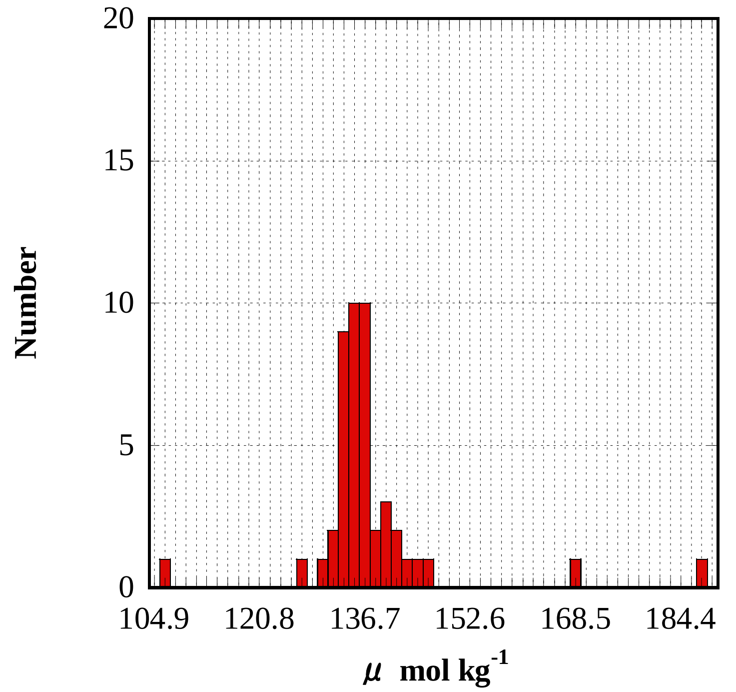


Figure A5-3 Silicate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of silicate concentration of sample #3 (lower panel)

Sample 4 Silicate

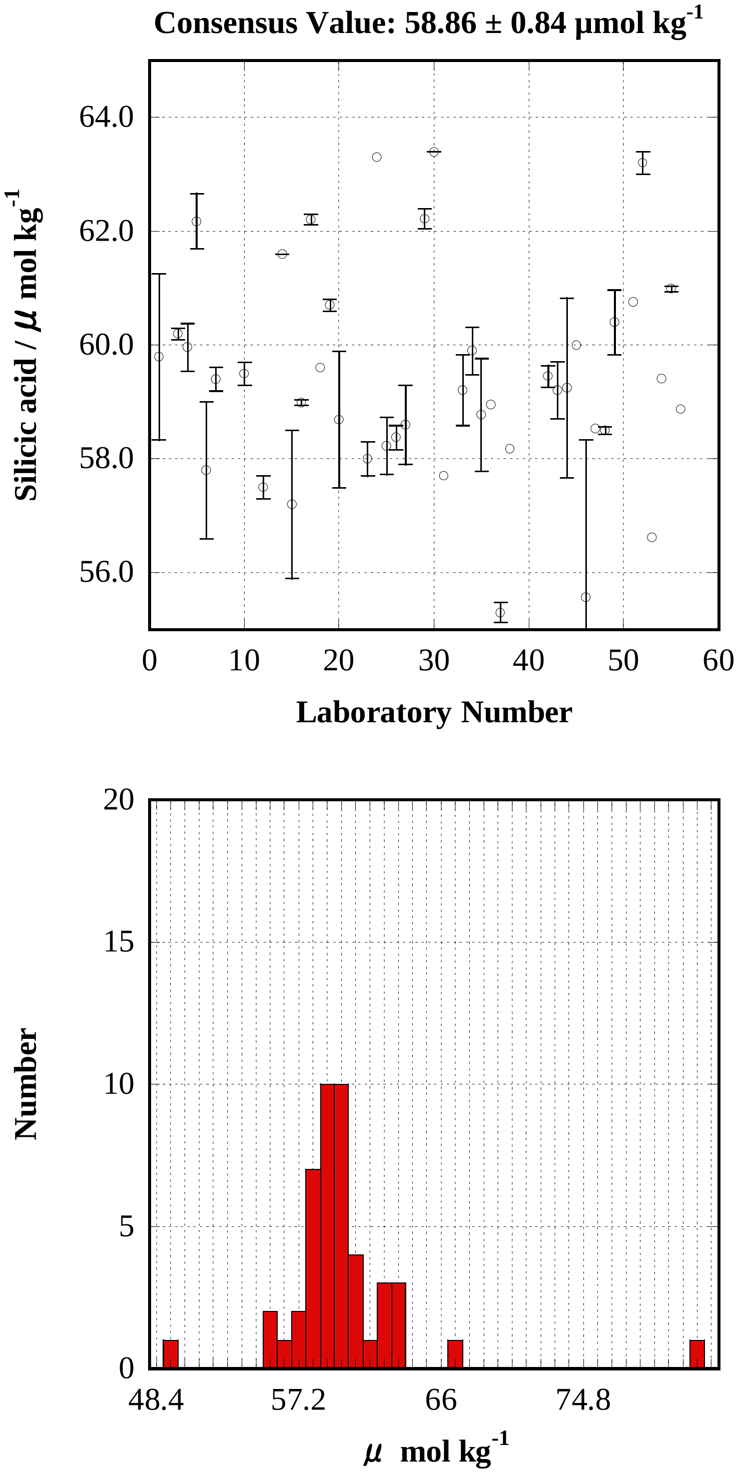


Figure A5-4 Silicate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of silicate concentration of sample #4 (lower panel)

Sample 5　Silicate

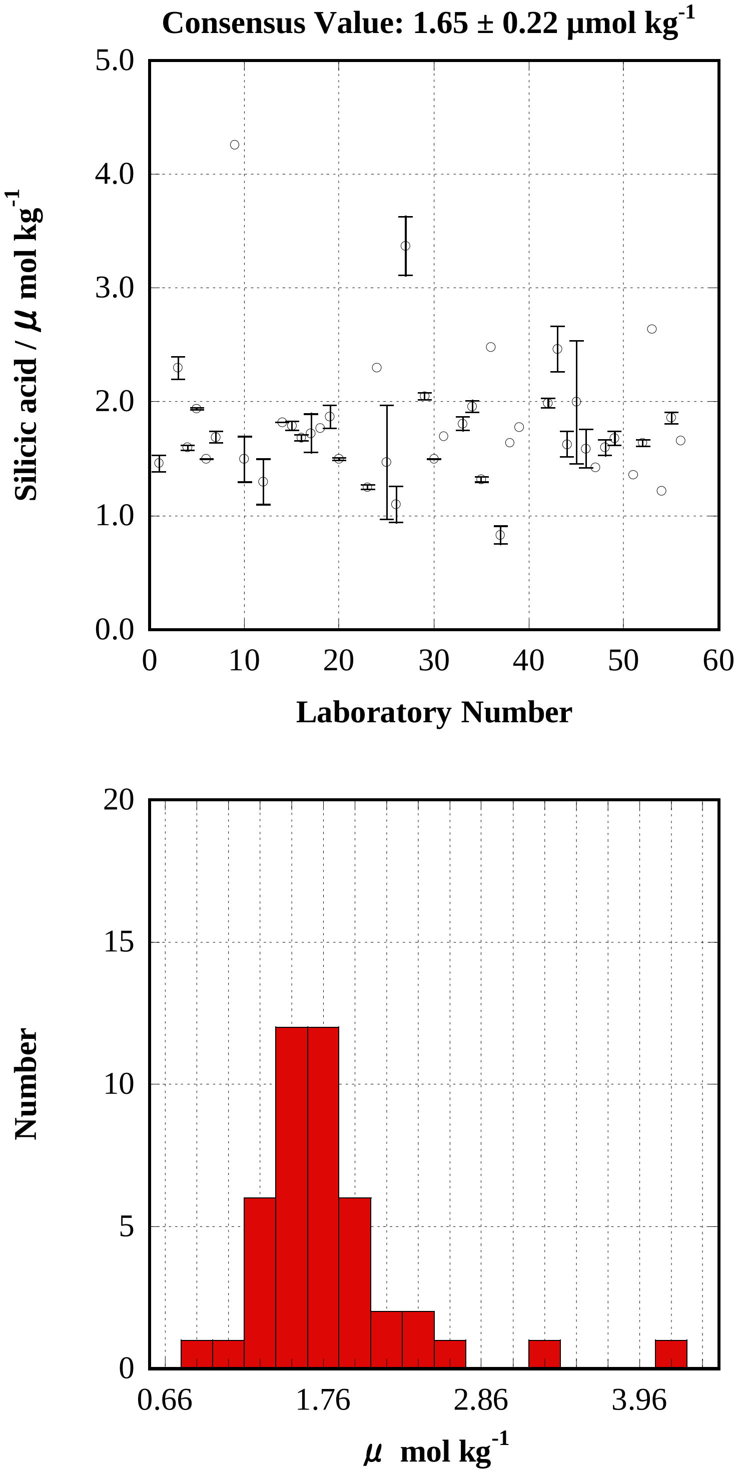
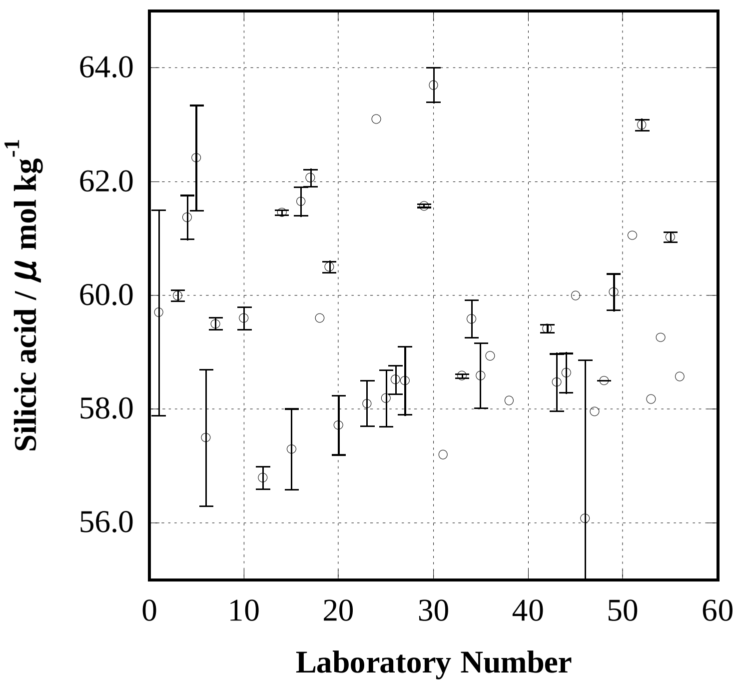


Figure A5-5 Silicate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of silicate concentration of sample #5 (lower panel)

Sample 6　Silicate

Consensus Value: 58.86 ± 0.84 μmol kg-1



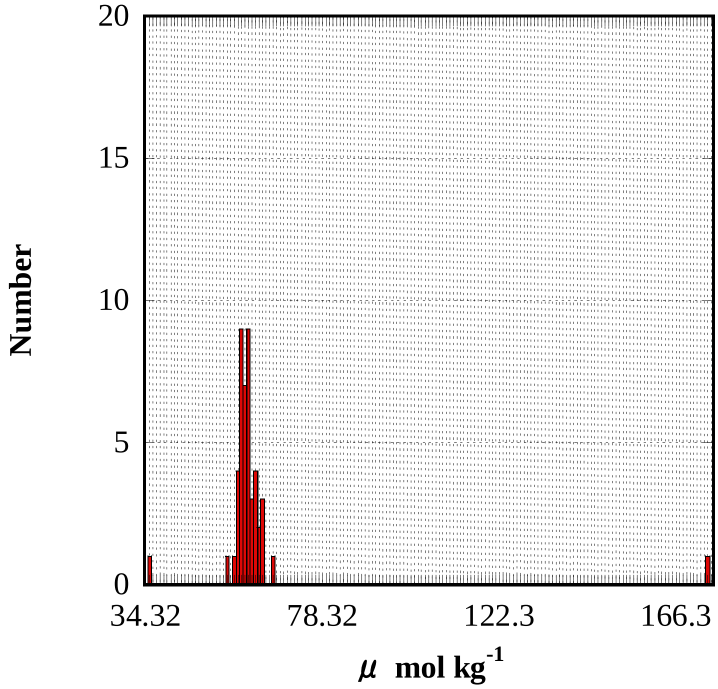


Figure A5-6 Silicate results: concentrations *versus* laboratory number (upper panel)
Frequency distribution of silicate concentration of sample #6 (lower panel)

Apendix IV

Documents

IV – 1 Call for participating

7 June 2006

Dear Colleague,

This letter is to invite you to “Inter-comparison study for Reference Material of Nutrients in Seawater in a seawater matrix 2006”.
The objective of this effort is to establish comparability on nutrient analyses in seawater among the laboratories/research vessles.

The “Group of Expert on standards and Reference Material” had stated (UNESCO, 1991,1992) the necessity of giving high priority to developing production of Reference Material of for Nutrients in Seawater (hereafter RMNS) and some researchers has been carrying out the studies to provide the certified RMNS. Along with the efforts to provide the certified RMNS, Inter-comparison studys of the nutrients in seawater has been carried out to establish comparability on nutrients analyses in seawater. The ICES nutrients Inter-comparisons were done five times since 1965 (UNESCO 1965, 1967; ICES 1967, 1977; Kirkwood et al., 1991, Aminot and Kirkwood, 1995). In 2000 and 2002, NOAA/NRC Inter-comparisons had carried out to certify the MOOS-1 (Willie and Clanay, 2000; Clanay and Willie, 2003). In 2003, “Inter-comparison study for Reference Material of for Nutrients in Seawater in a seawater matrix 2003” was done by Meteorological Research Institute (Aoyama, 2006, submitted). Six concentrations of the samples were distributed and a greater range was covered than in the previous Inter-comparisons. Those concentrations were 0-38 μmol kg^{-1} for nitrate, 0-0.9μmol kg^{-1} for nitrite, 0-2.7μmol kg^{-1} for phosphate and 0-136μmol kg^{-1} for silicate, respectively. A total of 18 sets of samples were distributed in 5 countries. Results were returned by 17 laboratories in 5 counties.

This “Inter-comparison study for Reference Material of Nutrients in Seawater in a seawater matrix 2006” is planned to make more progress in this field. This Inter-comparison has two advantages. First advantage is that the nutrients concentrations of the distributed samples would be set to cover the wider ranges of nutrients concentration rather than those in 2003 Inter-comparison. Second advantage is that method of preparation of the distributed samples for this Inter-comparison (Aoyama et al, 2006) becomes available to analyze four determinands, nitrate, nitrite, phosphate and silicic scid in one bottle simultaneously as natural seawater samples.

A reply sheet attached should be used to confirm your participation and following points should be clearly understood.

1, If you do not return the sheet by the end of July 2006, you will not receive any RMNS samples.

2, I will acknowledge receipt of your reply and list of the participants on 15 August 2006. If you do not receive an acknowledgement by 15 August 2006, please contact us in case your reply has gone elsewhere.

3, The reply sheet will confirm that your wish to participate this comparison exercise and to analyzing the samples and submitting results before the reporting deadline, 25 December 2006, or returning the samples intact before the reporting deadline, if for any reason you are unable to analyze them. I expect to receive nutrients concentrations for nitrate, nitrite, phosphate and silicate.

4, All results reported will be published with the name of data originator after the data in the publication is confirmed by each data originator.

Some documents are available at our web page http://www.mri-jma.go.jp/Dep/ge/RMNScomp.html and anonymous ftp site mri-2.mri-jma.go.jp. In the directory /pub/geochem/outgoing/rmns_comp in the anonymous ftp site, you will find and can download (set to binary mode, please) a draft of "Report of Inter-comparison study for Reference Material of for Nutrients in Seawater in a seawater matrix 2003".

Best regards,

Michio AOYAMA, Dr.
Senior Scientist
Geochemical Res. Dep.
Meteorological Research Institute
e-mail: maoyama@mri-jma.go.jp

Inter-comparison study for Reference Material of for Nutrients in Seawater in a seawater matrix 2006

IMPORTANT DATES

DEADLINE OF REPLY: 31 JULY 2006.

LIST OF PARTICIPANT: 15 AUGUST 2006.

SAMPLES SHIPPED BY : 15 SEPTEMBER 2006

REPORTING DEADLINE: 25 DECEMBER 2006

EXPECTED DRAFT OF INTER-COMPARISON SUMARY:
28 FEBRUARY 2006

PLEASE RETURN THIS SHEET TO kagaku22@mri-jma.go.jp

or mail to
Michio AOYAMA
Geochemical Res. Dep.
Meteorological Res. Inst.
1-1 Nagamine, Tsukuba,
305-0052 JAPAN

Inter-comparison study for Reference Material of for Nutrients in Seawater in a seawater matrix 2006

I have received your letter and now return this sheet to confirm my intention to participate.

Name:

Affiliation:

Full postal address to receive samples

E-mail

Date:

Your comment:

Note: You can download this format from http://www.mri-jma.go.jp/Dep/ge/RMNScomp.html

IV – 2 Instructions for RMNS bottles

Instructions for samples

1. Package contents
1) Your package contains 6 bottles
2) You will see the sample IDs, from sample1 to sample 6, and lab# with your name.

2. Preparations of samples
1) No preservatives have been added.
2) The details of preparation are given in a paper entitled “Reference material for nutrients in seawater in a seawater matrix”.

3. Analyses
1) Samples are ready for analyses, then please use them without filtration and just after you open the bottles. Again, no preservatives have been added, when opened their sterility will be lost.
2) Salinities of samples are as follows;

SAMPLE 1	34.63+-0.01
SAMPLE 2	34.33+-0.01
SAMPLE 3	34.45+-0.01
SAMPLE 4	34.45+-0.01
SAMPLE 5	34.62+-0.01
SAMPLE 6	34.45+-0.01

3) Concentrations of the nutrients can be assumed to be in the following ranges in micromoles per kilogram. Some people may be surprised by high concentrations of sample 2 and 3, however, these samples are Pacific origin.

	Nitrite	Nitrate	Nitrite+Nitrate	Phosphate	Silicic acid
SAMPLE 1	<1.0 ------------	<10 ------------		<1.0 ------------	<50 ------------
SAMPLE 2	<0.2 ------------	<45 ------------		<3.5 ------------	<170 ------------
SAMPLE 3	<0.2 ------------	<45 ------------		<3.5 ------------	<170 ------------
SAMPLE 4	<1.0 ------------	<25 ------------		<2.0 ------------	<100 ------------
SAMPLE 5	<0.2 ------------	<5 ------------		<0.5 ------------	<10 ------------
SAMPLE 6	<1.0 ------------	<25 ------------		<2.0 ------------	<100 ------------

4. Reporting of results
1) Report concentrations in micromoles per kilogram using the reporting format attached. You can have a file of a reporting format in the website of this Inter-comparison at MRI.

2) Please report one value for each parameter for each sample.
3) Participants are welcome to add your estimation on analytical uncertanity for each parameter for each sample (ex. 1.23±0.04; 23.45±0.67).
4) REPORTING DEADLINE: 25 December 2006

Appendix V

History of nutrient inter-laboratory comparison study

Appendix V History of nutrient inter-laboratory comparison studies

This history of nutrient inter-laboratory comparison studies is based on several reports from previous inter-laboratory comparison studies. The history of the first to fourth ICES exercises is included in Aminot and Kirkwood's (1995) detailed report of the fifth ICES inter-comparison. The results of the fifth ICES exercise and the first and second NOAA/NRC inter-comparisons are also summarized in this appendix.

1. First ICES exercise

The first inter-laboratory comparison study to include nutrients was a regional exercise conducted entirely in the Baltic Sea in June 1965, when the following three research vessels met by private agreement in Copenhagen:

Aranda	Institute of Marine Research (IMR), Helsinki
Hermann Wattenberg	Institut für Meereskunde, Kiel
Skagerak	Royal Fishery Board, Gothenburg

Each ship contributed freshly collected bulk samples, which were subsampled and analyzed on board each of the three participating ships on the same day. Oxygen, salinity, chlorinity, alkalinity, and phosphate were determined.

2. Second ICES exercise

The second ICES exercise, carried out in 1966 under the auspices of the newly formed ICES Working Group on the Intercalibration of Chemical Methods, was also predominantly a Baltic initiative and consisted of two parts: Part I, Leningrad, during the 5th Conference of Baltic Oceanographers (May 1966); and Part II, Copenhagen, at the 54th ICES Statutory Meeting (September 1966).

Part I

The following research vessels participated:

Alkor	Institut für Meereskunde, Kiel
Okeanograf	Institute of Marine Research, Leningrad
Prof Otto Krammel	Institut für Meereskunde, Warnemünde
Skagerak	Fisheries Board of Sweden, Gothenburg

Research vessels delivered bulk samples, which were subsampled and analyzed almost immediately for oxygen, salinity, chlorinity, pH, and phosphate.

Part II

The list of interested parties continued to grow, and in addition to Baltic countries, Norway and the UK were represented. Research vessels delivered bulk samples, and the participants analyzed the samples simultaneously while in Copenhagen. The determinands of primary interest included not only oxygen, salinity, chlorinity, and phosphate (as for Part I and the previous year's exercise in Copenhagen) but also nitrate, nitrite, and silicate.

The final report, edited by Grasshoff (UNESCO, 1966), makes no mention of nitrate or nitrite, but some of those who were present indicated that these results were "too terrible to be included"! To be fair to those involved, 1966 was early in the development of heterogeneous cadmium-based nitrate/nitrite reduction techniques, and some of the analytical problems were presumably not fully appreciated at that time.

Evidently nitrate analysis had some way to go to exhibit the reliability and ease of operation of the Murphy and Riley (1962) phosphate technique, but note that inter-laboratory comparison study on phosphate up until then had consisted of a series of simultaneous analyses of freshly obtained subsamples carried out by a few highly competent workers, working in close contact with one another and exchanging calibration solutions, ideas, technical details, and so on. Subsequent to the Copenhagen trials, Jones and Folkard (ICES, 1966) undertook a detailed laboratory examination of the individual methods used by the participants, and, in their contribution to Grasshoff's report, they announced, "There seems to be no need for any further intercalibration in the determination of inorganic phosphate by this method".

Clearly this happy state of affairs could and did not last. Along came the autoanalyzer!

3. Third ICES exercise

The third ICES exercise was organized by the ICES Working Group on Chemical Analysis of Sea Water under the joint auspices of ICES and SCOR, and its official title, "The International Intercalibration Exercise for Nutrient Methods 2", shows that it was an ambitious project.

Samples were distributed in 1969–1970, and 45 laboratories from 20 countries submitted results. The final report on the results of the exercise was not published for several years (ICES, 1977).

The time had come to study nutrients separately from oxygen, salinity, chlorinity, and pH, but with the awareness of the problems arising from the instability of natural seawater samples, the organizers chose to use standard solutions that were prepared and distributed by the Sagami Chemical Research Center, Japan. [*Note added by Aoyama*: The standard solutions used in this exercise were Cooperative Survey of Kuroshio (CSK) standards, which are solutions in artificial seawater for nitrate, phosphate, and silicate, and in pure water for nitrite.]

In this exercise, participants performed the analyses in their own laboratories, but despite the fact that the participants were aware that they had been supplied with appropriate blank solutions for each determination, the overall accuracy, particularly for phosphate and nitrate, was disappointing.

The report concludes, "As methods did not diverge much, it is clear that variations must be sought primarily in the standardization procedures. The results will also aid participants in re-evaluating their analytical procedures by comparison of their methods with those that appear most satisfactory from this exercise".

The names of the participating laboratories were listed, as were the tables of results, but it was not possible to link the names with the results. Hindsight suggests that the lack of such a link may have been counterproductive; we now suspect that there is no greater incentive for a laboratory to improve its performance than the knowledge that peer laboratories throughout the world will be made aware that it is producing poor-quality data.

4. Fourth ICES exercise

Various "workshop" and multiship events following the third ICES exercise included nutrient studies, but not until many years later (1988) did the ICES Marine Chemistry Working Group produce volunteers (Don Kirkwood, Alain Aminot, and Matti Perttilä) to organize the next large-scale inter-calibration exercise, designated NUTS I/C 4. This exercise did not set out to be global; it began only with laboratories in ICES member countries, but other laboratories that were interested in participating were not turned away.

The fourth exercise differed from the third in three important respects:

1) The test samples were natural or near-natural seawater rather than standard solutions. (Strictly speaking, this made the exercise an inter-comparison rather than an inter-calibration.)
2) Participants were unaware that blank samples had been included.
3) Anonymity was abolished. Participants were made aware from the outset that the final report would list identities of laboratories, results, and contact information for the participants.

Sixty-nine laboratories from 22 countries submitted results and, thanks in some measure to the telefax machine, the final 83-page report (Kirkwood et al., 1991) was in the hands of participants within two years of the distribution of samples. Statistical treatment identified 58 laboratories consistent in phosphate analyses, 51 consistent in nitrate analyses, and 48 consistent in both phosphate and nitrate analyses, including a group of 12 whose results were especially close to the consensus concentrations.

5. Fifth ICES exercise

Owing to the generally perceived need for more and better quality control in analytical measurement, a fifth ICES inter-laboratory comparison study was carried out in 1993. A total of 142 sets of samples were distributed in 31 countries. Results were returned by 132 laboratories, 61 of which had participated in the fourth inter-comparison and 56 of which were participating in Quality Assurance of Information for Marine

Environmental Monitoring in Europe. The distribution of the laboratories was as follows: UK (22), Germany (18), Sweden (13), France (11), Spain (8), USA (7), Norway (5), Ireland (5), Australia (4) Canada (4), Netherlands (4), Denmark (3), Greece (3), Portugal (3), Belgium (2), Estonia (2), Finland (2), Italy (2), Poland (2), Argentina (1), Bermuda (1), China (1), Faroe Islands (1), Iceland (1), Japan (1), Latvia (1), Lithuania (1), New Zealand (1), Qatar (1), South Africa (1), and Turkey (1)

The method of sample preparation—autoclaving—for the fifth exercise imposed constraints that resulted in there being only two relevant determinands per sample (nitrate and nitrite in one series, and phosphate and ammonia in the other series).

A large volume of low-nutrient natural seawater was spiked with known concentrations of nutrient salts. Although the concentrations in the distributed samples covered a greater concentration range than the concentrations in the fourth exercise, the concentration levels in the fifth exercise were chosen as representative of the Atlantic Ocean: 1–26 μmol L^{-1} for nitrate and 0.08–1.85 μmol L^{-1} for phosphate.

6. 2000 NOAA/NRC inter-comparison

The test material distributed in this inter-comparison was MOOS-1, a proposed reference material for nutrients in seawater (Clancy and Willie, 2004). The sample material was intended to be a certified reference material for silicate, phosphate, nitrite, and nitrate+nitrite. Participating laboratories were each sent two bottles of MOOS-1 and asked to perform duplicate analyses on each of the bottles. The prepared samples were sent to 36 participating laboratories, and 30 sets of results were returned.

The results of this inter-comparison may, in several respects, have been compromised by sample homogeneity problems. The target standard deviation for measuring *p*-scores was too broad and did not reflect the measurement precision that could be attained.

7. 2002 NOAA/NRC inter-comparison

An inter-laboratory comparison study was undertaken to assess the current capabilities of a group of laboratories to quantitate orthophosphate, silicate, nitrite, and nitrate+nitrite in a seawater sample. This was the second such exercise sponsored by the NOAA Center for Coastal Monitoring and Assessment (CCMA), and the exercise was coordinated by the Institute for National Measurement Standards of the National Research Council Canada. Two seawater samples—one from Pensacola Sound, Florida, and a proposed certified reference material for nutrients in seawater (MOOS-1)—were distributed to 31 laboratories. Twenty-four laboratories submitted data. Methodologies were not prescribed to the participants; however, all reported results were obtained using traditional colorimetric procedures. Generally, satisfactory agreement among participants was achieved, with results within 10% of the assigned mean values.

The results from this exercise suggest that the homogeneity problem identified in the first NOAA/NRC inter-laboratory comparison study was overcome, although the orthophosphate data indicated a larger inter-laboratory spread of results than expected.

Results for silicate, nitrite, and nitrate+nitrite in the distributed seawater samples were acceptable for the majority of the participants and generally deviated by less than ±10% from the assigned mean. All laboratories used methodologies based on colorimetric principles.

8. 2003 MRI inter-comparison

Six batches of the RMNS used for the inter-laboratory comparison study were produced in 2001 and 2002 and were sent to participants (18 laboratories from five countries) in 2002. One sample from each batch, that is, six samples in total, was distributed to individual laboratories. For shipping to each laboratory, we used normal commercial transportation. No serious damage to samples during the transportation was reported, although one laboratory reported shortage of the samples.

One group cancelled its participation in the exercise, so the final number of laboratories was 17. All results from the 17 laboratories were received by April 2003. One group did not report nitrite. Four laboratories did not report nitrate; instead they reported nitrate+nitrite. In such cases, concentrations of nitrate were calculated by subtracting concentrations of nitrite from those of nitrate+nitrite. Four laboratories did not report silicate.

Results of the inter-laboratory comparison study presented contemporary inter-laboratory comparability of nutrient data; standard deviations of phosphate and silicate, which represent the overall discrepancy of reported values, were 4.5 times and more than 10 times, respectively, the corresponding homogeneities of the RMNS prepared for the study. For nitrate, the standard deviation was only ~2 times as great as the homogeneity. These results demonstrate that for nitrate, our community is using analytical techniques good enough to provide data of high comparability. These results also indicate that variability of the in-house standards of the participating laboratories—rather than analytical precision—is the primary source of the inter-laboratory discrepancy. Therefore, the use of a certified reference material for nutrients in seawater is essential for establishing nutrient data sets that can be compared across laboratories, especially for silicate and phosphate in seawater.

8. 2006 MRI inter-comparison

Autoclaved natural seawater was used for an inter-laboratory comparison study for a reference material for nutrients in seawater in 2006; this study was similar to the 2003 inter-laboratory comparison study. Sample homogeneity was confirmed by the repeatability of the measurements: for nitrate, phosphate and silicate, the homogeneities were 0.22%, 0.32% and 0.19%, respectively. Sets of six samples covered concentration ranges of 0.1–42.4 μmol kg^{-1} for nitrate, 0.0–0.6 μmol kg^{-1} for nitrite, 0.0–3.0 μmol kg^{-1} for phosphate, and 1.7–156.1 μmol kg^{-1} for silicate. A set of samples was distributed to each of 55 laboratories in 20 countries. Results were returned by 52 laboratories in 19 countries.