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栄養塩測定用海水組成標準の2003年国際共同実験報告

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Preface

The analysis of nitrate, nitrite, phosphate, and silicic acid, in seawater has been carried out for more than 50 years. The concentrations of nutrients in seawater are important for various oceanographic uses. The climatological distribution of nutrients in the ocean has been established over the past 4 decades. In the 1990s, accurate concentration data for nutrients in seawater were required by oceanographers to detect the temporal variability of ocean nutrients derived from climate change. Although high-accuracy, high-precision methods for nutrient analysis were available in the 1990s, such methods were not applied to analysis of nutrients in seawater, primarily because of a lack of a suitable reference material. In this study, Aoyama et al. have succeeded in preparing a reference material based on natural seawater. This reference material has passed homogeneity and long-term stability tests. To evaluate the reference material, an intercomparison between 18 laboratories was conducted. The results of the intercomparison, summarized in this report, indicate that a reference material is needed to establish traceability of nutrient data from laboratories and that comparable nutrient data sets sufficient for detecting variability can be established in the field of oceanography.

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Abstract

Autoclaved natural seawater was used to prepare samples for an interlaboratory comparison exercise for a reference material for nutrients in seawater. Sample homogeneity was confirmed by repeatability of measurement. Sets of 6 samples covering a concentration range greater than that in previous intercomparisons were prepared. Concentrations were 0 –38 µmol kg^{-1} for nitrate, 0.0–0.9 µmol kg^{-1} for nitrite, 0.1–2.7 µmol kg^{-1} for phosphate, and 2–136 µmol kg^{-1} for silicic acid. A total of 18 sets of samples were distributed to 18 laboratories in 5 countries. Results were returned by 17 laboratories in 5 countries. Although consensus concentrations were obtained for the 6 samples, the standard deviations were 4.5 times and more than 10 times greater than those of the homogeneities for phosphate and silicic acid, respectively. For nitrate, the standard deviations were only about double the homogeneities. These results indicate that variability in in-house standards of the participating laboratories — rather than analytical precision — is the primary source of interlaboratory discrepancy. Therefore 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 silicic acid and phosphate in seawater.

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1. Introduction

The objective of this effort was to develop a reference standard for analysis of nutrients in seawater that would ensure comparability of analytical data collected by different laboratories and facilitate onboard analysis of nutrients in seawater. Highly accurate nutrient data could thus become available. We have focused on developing a certified reference material for nutrients in seawater in a seawater matrix. The IOC–IAEA–UNEP Group of Experts on Standards and Reference Materials (UNESCO, 1991, 1992) have clearly stated the need to place a high priority on developing a reference material for nutrients in seawater (hereafter RMNS).

Currently, the only way to ensure comparability among nutrient analyses performed by different laboratories is to conduct interlaboratory comparison experiments that provide consensus values plus uncertainties for nutrient concentrations. The ICES Nutrient Intercomparison has been done 5 times since 1965 (UNESCO, 1965, 1967; ICES, 1967, 1977; Kirkwood et al., 1991; Aminot and Kirkwood, 1995), and efforts to ensure comparability among analyses in this field have been carried out for 30 years. In 2000 and 2002, NOAA/NRC intercomparisons between laboratories in the United States and Canada were carried out to certify a seawater certified reference material for nutrients as MOOS-1 provided by National Research Council Canada (Willie and Clancy, 2000; Clancy and Willie, 2003). The first certified reference material for nutrients in seawater in a seawater matrix was provided as MOOS-1 in 2003 by the National Research Council of Canada (Clancy and Willie, 2004). However, the nutrient concentrations of MOOS-1 were too low for analysis of nutrients in Pacific Ocean seawater and did not cover the concentrations of nutrients in other seawater samples.

Thus, in 2003 the present exercise was planned and conducted to make progress in this field. This intercomparison has two advantages over previous intercomparisons. First, nutrient concentrations of the distributed samples were set to cover the concentration range of nutrients in the Pacific Ocean, which has the highest nutrient concentrations among the open oceans of the world. Second, the distributed samples were prepared in a natural seawater matrix in a single bottle so that 4 determinands (nitrate, nitrite, phosphate, and silicic acid) could be simultaneously analyzed.

This report describes the exercise in detail and summarizes the results reported by the participants.

2. Samples

2.1 Sample preparation and timetable for intercomparison

Progress in preparing RMNS samples has been made over the past 10 years (Aoyama et al., 2006). For this study, seawater in a stainless steel container (volume 40 to 200 L) was autoclaved twice at 120 ºC for 2 h. A sample for analysis consisted of 90 mL of the autoclaved seawater in a polypropylene bottle. This procedure for preparing samples is based on a previously reported method for preparing a reference material for the determination of nutrients in seawater (Aminot and Kerouel, 1991, 1995). Sample homogeneity was confirmed by repeatability of measurement. Long-term storage of our RMNS samples for up to 4 years showed that the homogeneities and concentrations of nutrients were maintained for about 4 years (Aoyama et al., 2006).

The samples sent to the participants were prepared in 2001 and 2002. The nutrient concentrations in the samples were confirmed to be stable for at least several months before the samples were sent to the participants between March 2002 and December 2002. All participants had analyzed the samples and returned their results by April 2003.

2.2 Selection of determinands

The determinands of interest were Nitrate (or Nitrate + Nitrite), Nitrite, Phosphate, and Silicic acid.

2.3 Sample homogeneity

The homogeneities of the samples were measured separately. The homogeneities for 30 bottles of sample 3 are listed in table 1. Analytical precision was also estimated for 30 samples of natural seawater whose nutrient concentrations were similar to those of sample 3.

Table 1 Homogeneity of sample 3 and analytical precision

	Nitrate + nitrite	Phosphate	Silicic acid
Homogeneity of sample 3 (%)	0.44	0.80	0.15
Analytical precision (CV %)	0.34	0.32	0.16

Note: The concentrations of nutrients in natural seawater for the simultaneous analyses were 43 μmol kg^{-1} for nitrate + nitrite, 3.1 μmol kg^{-1} for phosphate, and 148 μmol kg^{-1} for silicic acid.

Figure 1 Samples sent to participants

For sample 3, the homogeneities for nitrate + nitrite, phosphate, and silicic acid were good considering the analytical precision for the analysis of natural seawater (table 1). Since the concentrations of nutrients in sample 3 were similar to those in the natural seawater used in this study, the homogeneities for nitrate + nitrite and silicic acid were of the same order of magnitude as, or better than, the analytical precision. The homogeneity for phosphate had a larger scattering, which was attributed to the nature of the RMNS sample itself, and not any analytical problem.

Samples 1, 2, 4, 5, and 6 were not analyzed due to a limited number of samples. It is, however, safe to assume that these samples were similar in nature to sample 3, since all samples were prepared by the same process.

3. Participants and response

By November 2002, 18 laboratories in 5 countries had replied to the call for participants. A total of 18 sets of samples were distributed. Appendix I lists the participants.

Results were submitted by 17 laboratories; a set of samples was returned by 1 laboratory because it was unable to meet the deadline for submission of results. One participant did not report results for nitrite. Four participants did not report results for nitrate, but did report results for nitrate + nitrite. In these cases, nitrate concentrations were calculated from the nitrate + nitrite and nitrite concentrations. Four participants did not report results for silicic acid.

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	15	16
	2	15	17
	3	15	17
	4	15	16
	5	15	17
	6	15	17
Nitrite	1	16	15
	2	16	16
	3	16	14
	4	16	14
	5	16	16
	6	16	16
Nitrate	1	13	15
	2	13	16
	3	13	15
	4	13	15
	5	13	16
	6	13	16
Phosphate	1	17	17
	2	17	17
	3	17	17
	4	17	17
	5	17	17
	6	17	17
Silicic acid	1	13	13
	2	13	13
	3	13	13
	4	13	13
	5	13	13
	6	13	13

4. Statistical treatment

4.1 Consensus mean, median, and standard deviation

Successive *t*-tests at the 95% confidence level were applied to the results to remove outliers before estimating the consensus mean, median, and standard deviation. Tests were applied until a stable mean was reached, and stable means were obtained at the second test for all sets of results.

4.2 Calculation of *Z*-scores

Z-scores were used to evaluate the performance of laboratories.

The *Z*-score for each analysis is defined as

$$Z_{\mathrm{par}} = \mathrm{ABS}((C_{\mathrm{par}} - C_{\mathrm{consensus}})/P_{\mathrm{par}}) \qquad (1)$$

where Z_{par} is the *Z*-score for an analysis; C_{par} is the concentration of an RMNS sample measured by a laboratory for the parameter of interest (nitrate, phosphate, or silicate); $C_{\mathrm{consensus}}$ is the consensus sample concentration for the parameter of interest, described in section 4.1; and P_{par} is the standard deviation at the sample concentration for the parameter of interest.

Averages of the *Z*-scores for the 6 samples were calculated for nitrate ($Z_{\mathrm{NO_3}}$), nitrite ($Z_{\mathrm{NO_2}}$), phosphate (Z_{p}), and silicic acid (Z_{s}).

Averages of *Z*-scores for each laboratory were calculated for $Z_{\mathrm{NO_3}} + Z_{\mathrm{p}}$ and $Z_{\mathrm{NO_3}} + Z_{\mathrm{p}} + Z_{\mathrm{s}}$.

5. Results

5.1 Raw results

Results reported by the participants are summarized in Appendix II.

5.2 Consensus medians, means, and standard deviations

The consensus medians, means, and standard deviations (table 3) were calculated using the data that passed the successive *t*-test applications described in section 4.1. The consensus means and medians are in excellent agreement for all parameters for all samples.

Table 3 Consensus medians, means, and standard deviations for the 6 samples

	Nitrite (μmol kg^{-1})			**Nitrate (μmol kg^{-1})**			**Nitrate + nitrite (μmol kg^{-1})**		
Sample	**Median**	**Mean**	**SD**	**Median**	**Mean**	**SD**	**Median**	**Mean**	**SD**
1	0.02	0.02	0.01	0.05	0.04	0.03	0.07	0.06	0.04
2	0.14	0.13	0.06	17.5	17.4	0.7	17.7	17.6	0.6
3	0.01	0.01	0.01	35.4	35.3	0.3	35.4	35.4	0.3
4	0.02	0.02	0.02	0.02	0.02	0.03	0.04	0.04	0.04
5	0.90	0.91	0.02	13.0	13.1	0.2	14.0	14.0	0.2
6	0.24	0.23	0.09	38.4	38.2	1.1	38.5	38.4	1.0

	Phosphate (μmol kg^{-1})			**Silicic acid (μmol kg^{-1})**		
Sample	**Median**	**Mean**	**SD**	**Median**	**Mean**	**SD**
1	0.09	0.09	0.02	2.03	2.06	0.23
2	1.25	1.25	0.04	66.3	66.4	2.0
3	2.14	2.14	0.07	136.0	135.7	2.3
4	0.09	0.09	0.03	2.09	2.09	0.31
5	1.10	1.10	0.04	73.4	73.8	2.4
6	2.74	2.74	0.10	134.0	133.8	2.5

5.3 Scatter plots and histograms of the results

Scatter plots for nitrate, phosphate, and silicic acid are shown in figures 2–4, respectively. For nitrate and phosphate, laboratories were sorted by order of reported concentration of nitrate and phosphate in sample 6, for which the nitrate and phosphate concentrations were the highest in the 6 samples sent to the participants. For silicic acid, laboratories were sorted by order of reported silicic acid concentration in sample 3, for which the silicic acid concentration was the highest in the 6 samples. In figures 2–4, error bars appear when they were reported.

Scatter plots and histograms for each parameter of each sample are shown in figures 5-1 to 9-6. The consensus value is shown at the top of each figure. In the scatter plots, error bars appear when they were reported. Each histogram interval is set to equal the corresponding standard deviation shown in table 4.

5.4 Comparison between consensus standard deviation of sample 3 and homogeneity of sample 3

For nitrate, the consensus standard deviations were only about double the homogeneities (table 4). For phosphate, the consensus standard deviations were 4.5 times greater than that of the homogeneities, and for silicic acid, the consensus standard deviation was more than 10 times greater than that of the homogeneities.

Table 4 Comparison between consensus standard deviation of sample 3 and homogeneity of sample 3

	Nitrate	**Phosphate**	**Silicic acid**
Homogeneity (%)	0.44	0.80	0.15
Standard deviation (CV %)	1.0	3.5	1.7

5.5 *Z*-scores

Z-scores, computed according to the method described in section 4.2, are summarized in table 5.

Laboratories 3, 5, 6, and 15 showed consistently good performance throughout the range of nutrients.

Table 5 Summary of *Z*-scores

Laboratory	Z_{NO_3}	Z_{NO_2}	Z_p	Z_s	$(Z_{NO_3}+Z_p)/2$	$(Z_{NO_3}+Z_p+Z_s)/3$
1	22.97	2.07	1.02	1.34	11.99	8.44
2	3.71	1.43	1.24	6.04	2.48	3.66
3	0.37	0.44	0.41	0.65	0.39	0.48
4	1.02	0.63	0.97	0.52	1.00	0.84
5	0.46	0.41	0.95	no data	0.71	not available
6	0.33	0.39	0.63	0.08	0.48	0.35
7	0.71	0.77	1.16	0.96	0.93	0.94
8	0.90	0.97	0.38	1.02	0.64	0.77
9	0.58	0.77	2.12	1.80	1.35	1.50
10	1.02	1.46	0.68	no data	0.85	not available
11	2.13	0.96	0.77	0.63	1.45	1.18
13	0.69	0.50	0.61	1.27	0.65	0.86
14	0.86	1.08	1.19	no data	1.02	not available
15	0.89	0.81	0.78	no data	0.83	not available
16	1.19	0.84	2.28	0.79	1.74	1.42
17	2.65	1.84	0.65	0.53	1.65	1.27
18	0.36*	no data	0.96	2.58	0.66	1.30

*Z_{NO_3} for this laboratory was not available; the listed value corresponds to $Z_{NO_3+NO_2}$.

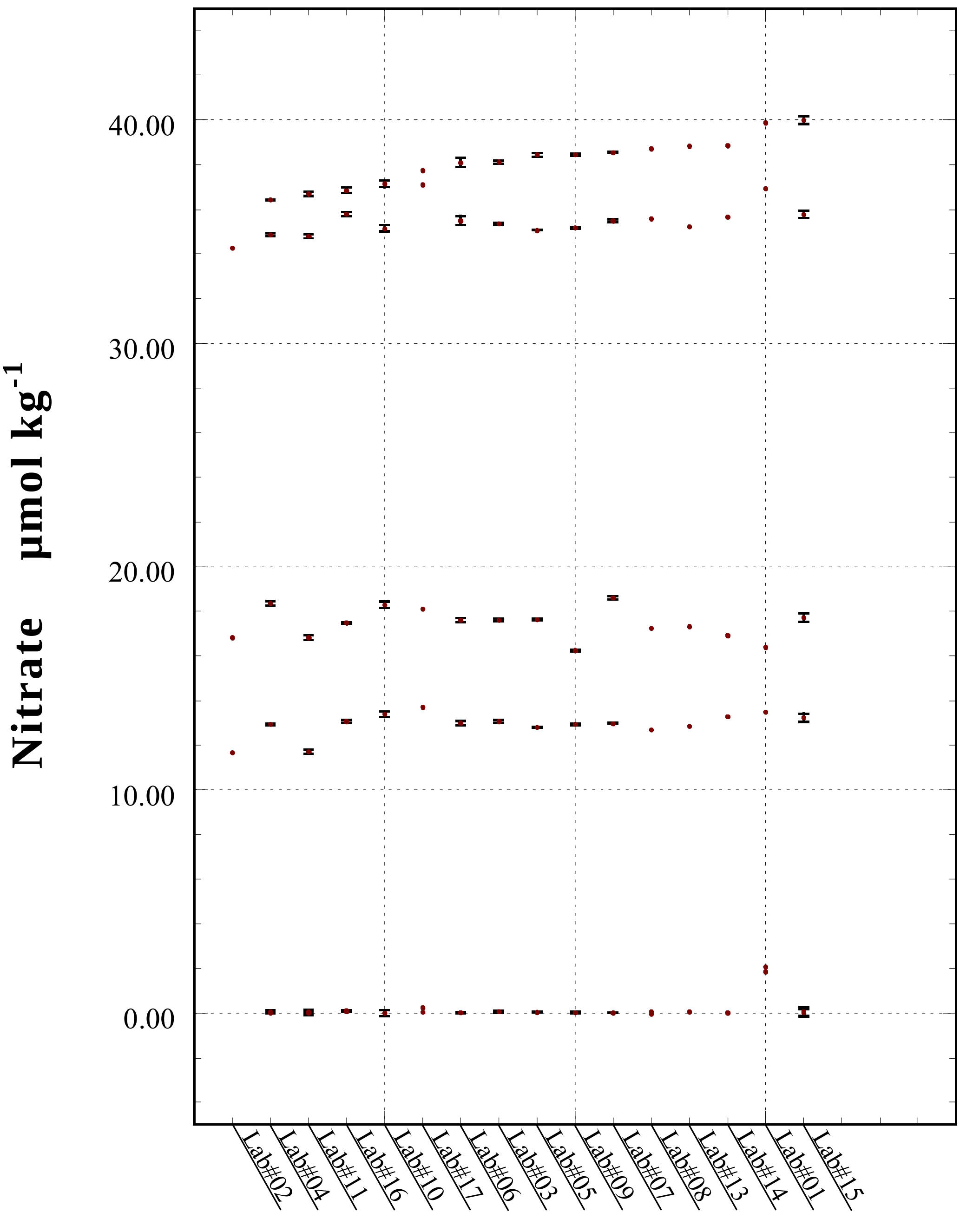


Figure 2 Nitrate results for sample 6: concentration *versus* laboratory number sorted by concentration.

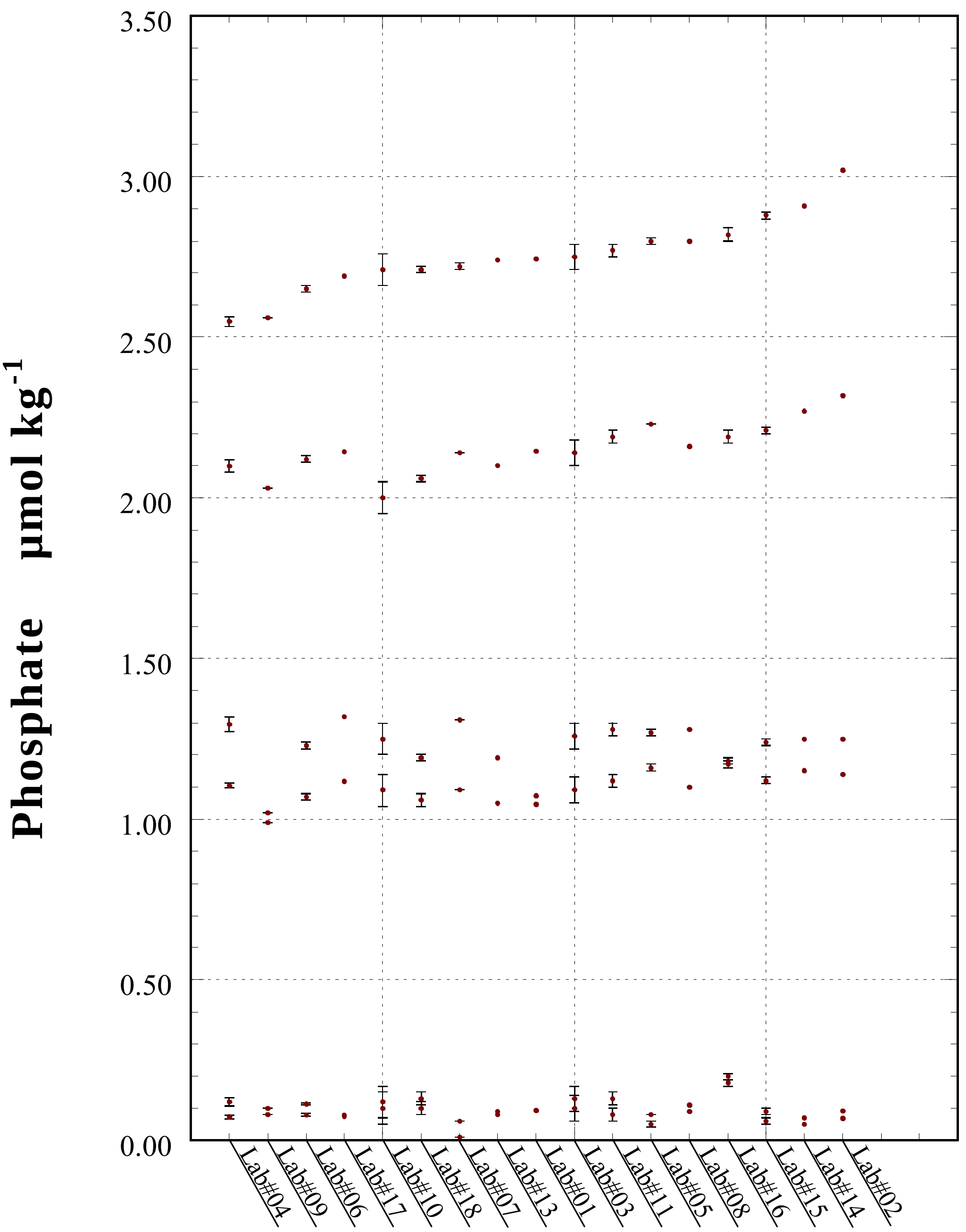


Figure 3 Phosphate results for sample 6: concentration *versus* laboratory number sorted by concentration.

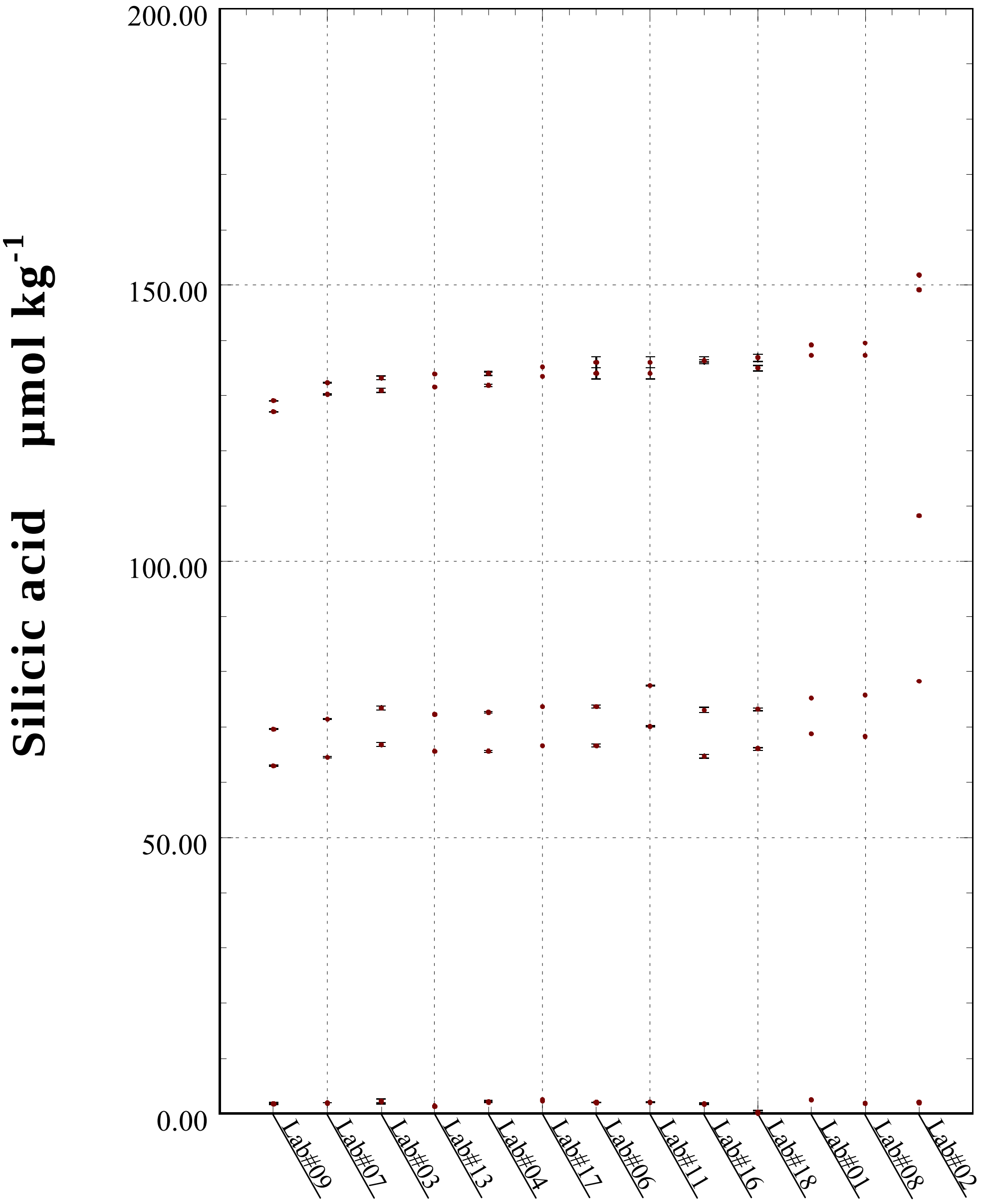


Figure 4 Silicic acid results for sample 3: concentration *versus* laboratory number sorted by concentration.

Sample 1 — Nitrite

Consensus Value: 0.02 ± 0.01 µmol kg^{-1}

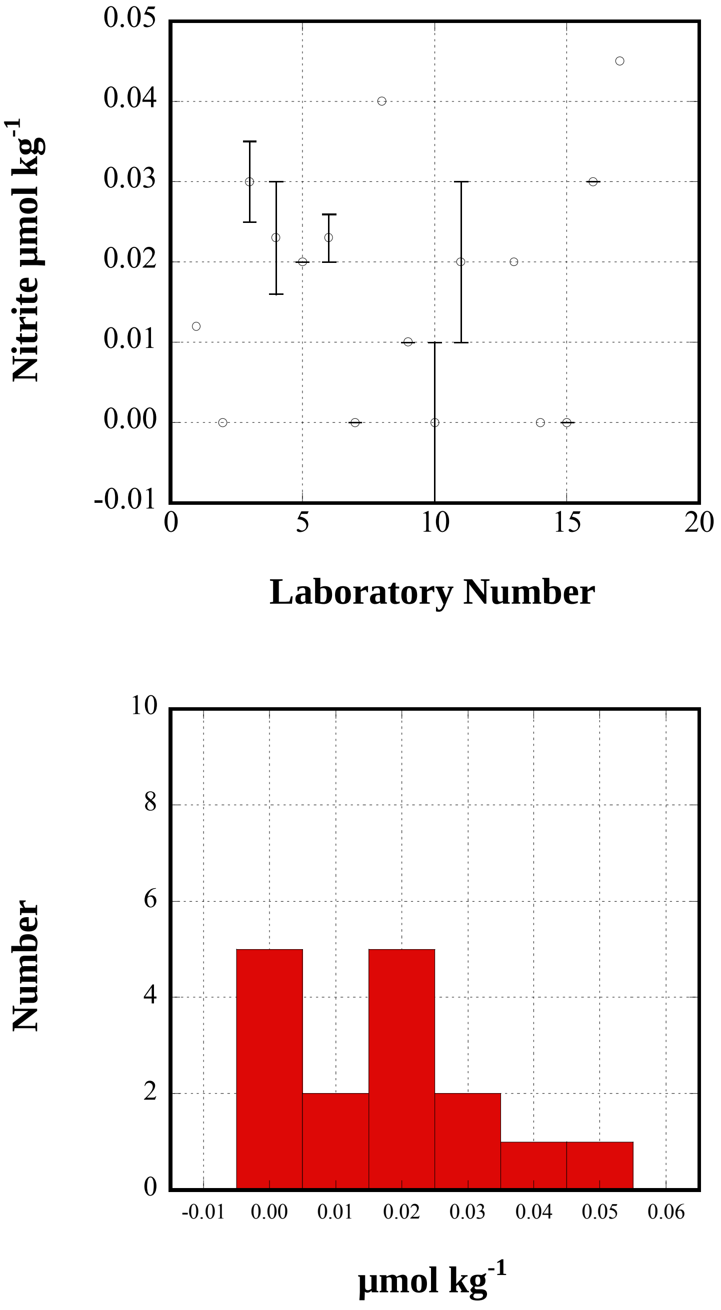
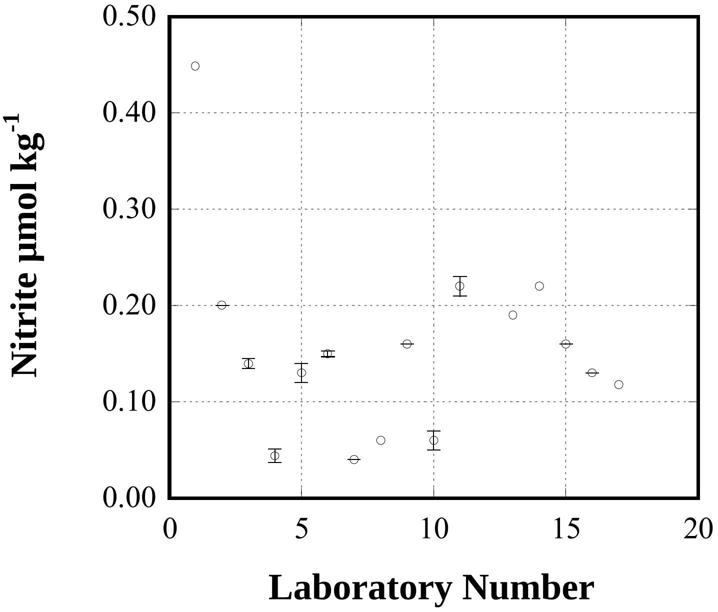


Figure 5-1 Nitrite results for sample 1: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 2 — Nitrite

Consensus Value: 0.13 ± 0.06 µmol kg^{-1}



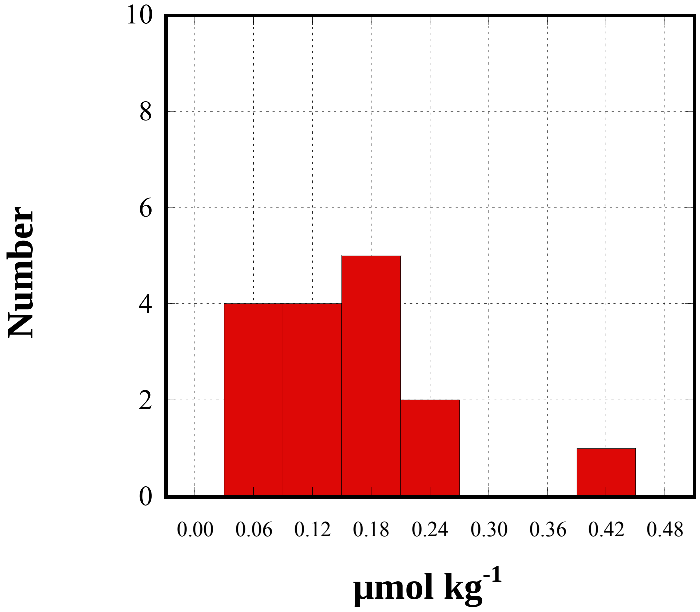
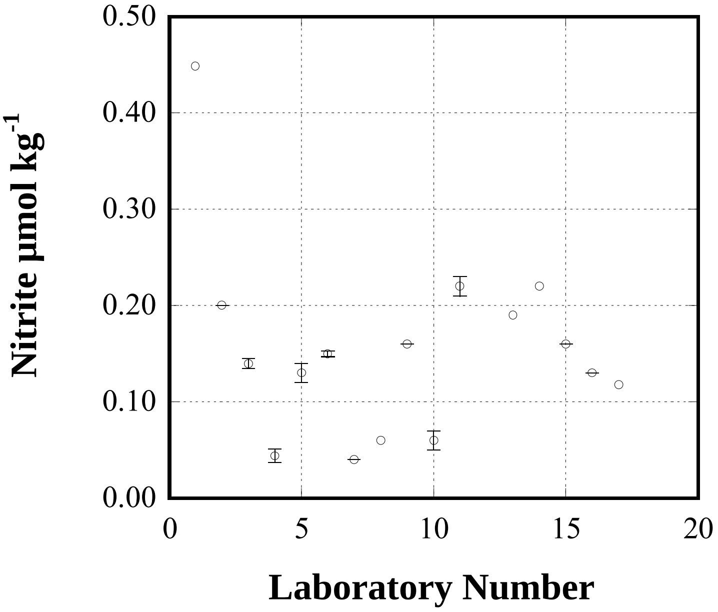


Figure 5-2 Nitrite results for sample 2: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 3 — Nitrite

Consensus Value: 0.01 ± 0.01 µmol kg^{-1}



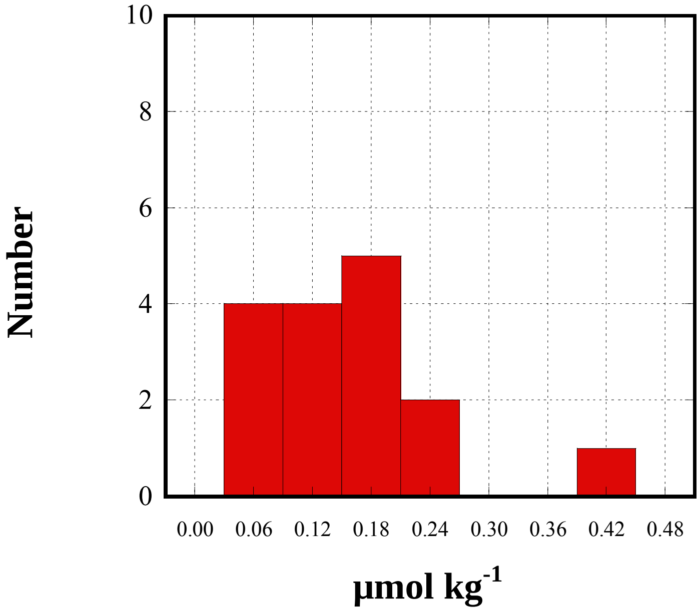
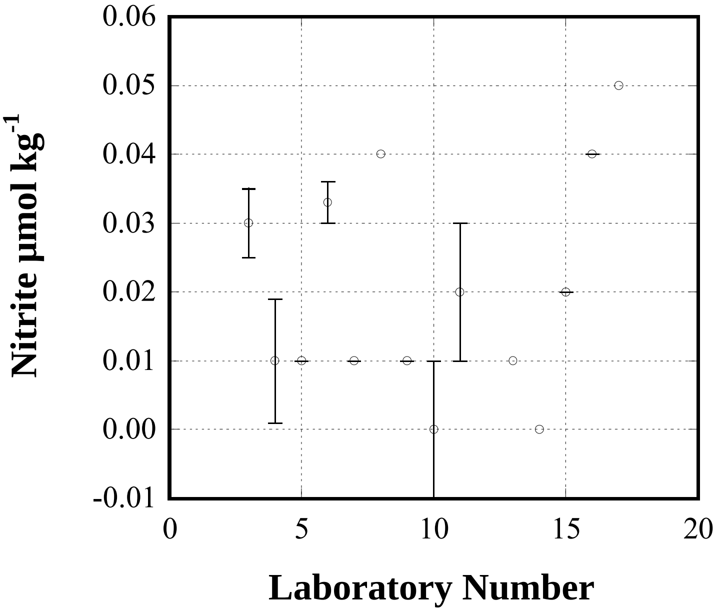


Figure 5-3 Nitrite results for sample 3: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 4 — Nitrite

Consensus Value: 0.02 ± 0.02 μmol kg^{-1}



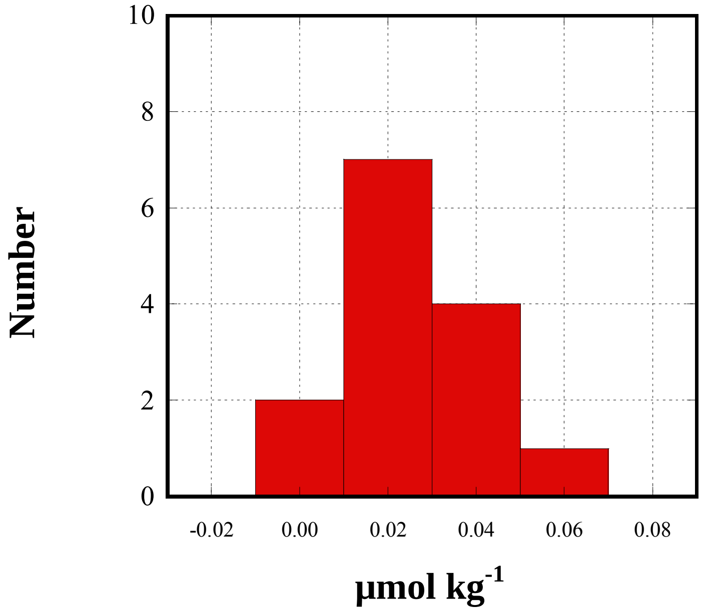


Figure 5-4 Nitrite results for sample 4: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 5 — Nitrite

Consensus Value: 0.91 ± 0.02 µmol kg^{-1}

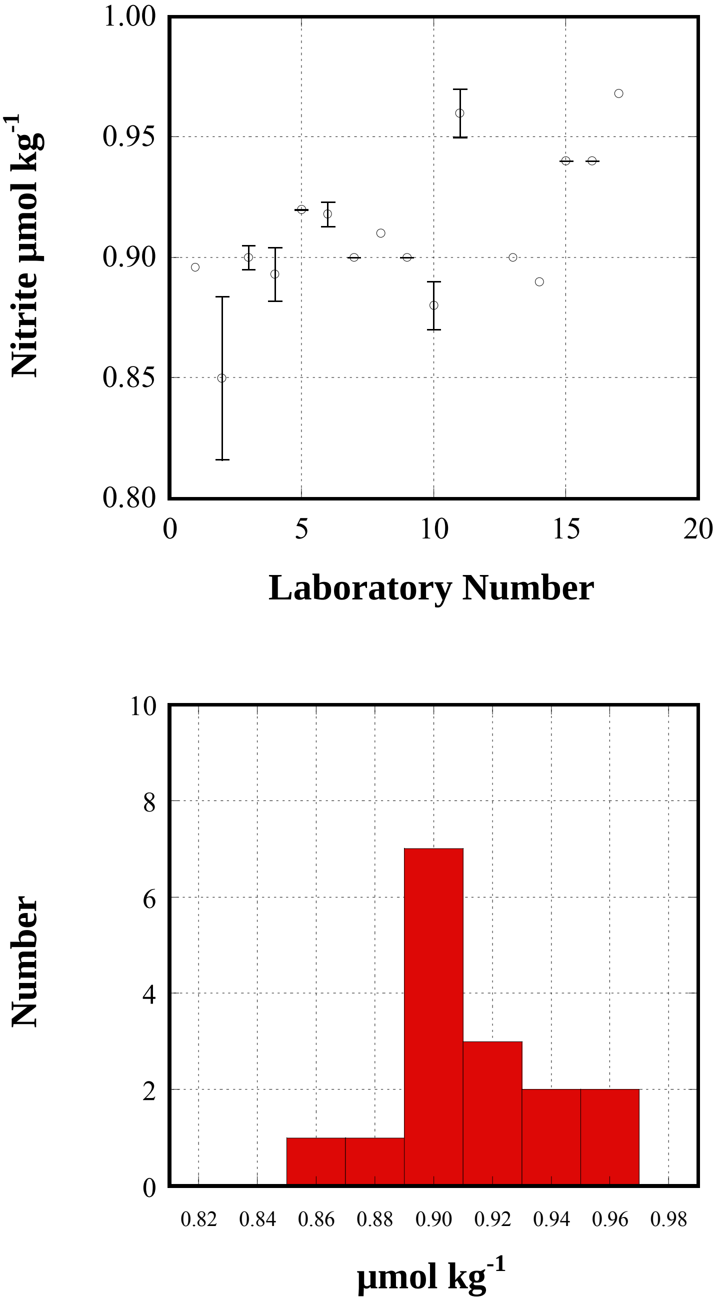


Figure 5-5 Nitrite results for sample 5: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 6 — Nitrite

Consensus Value: 0.23 ± 0.09 µmol kg^{-1}

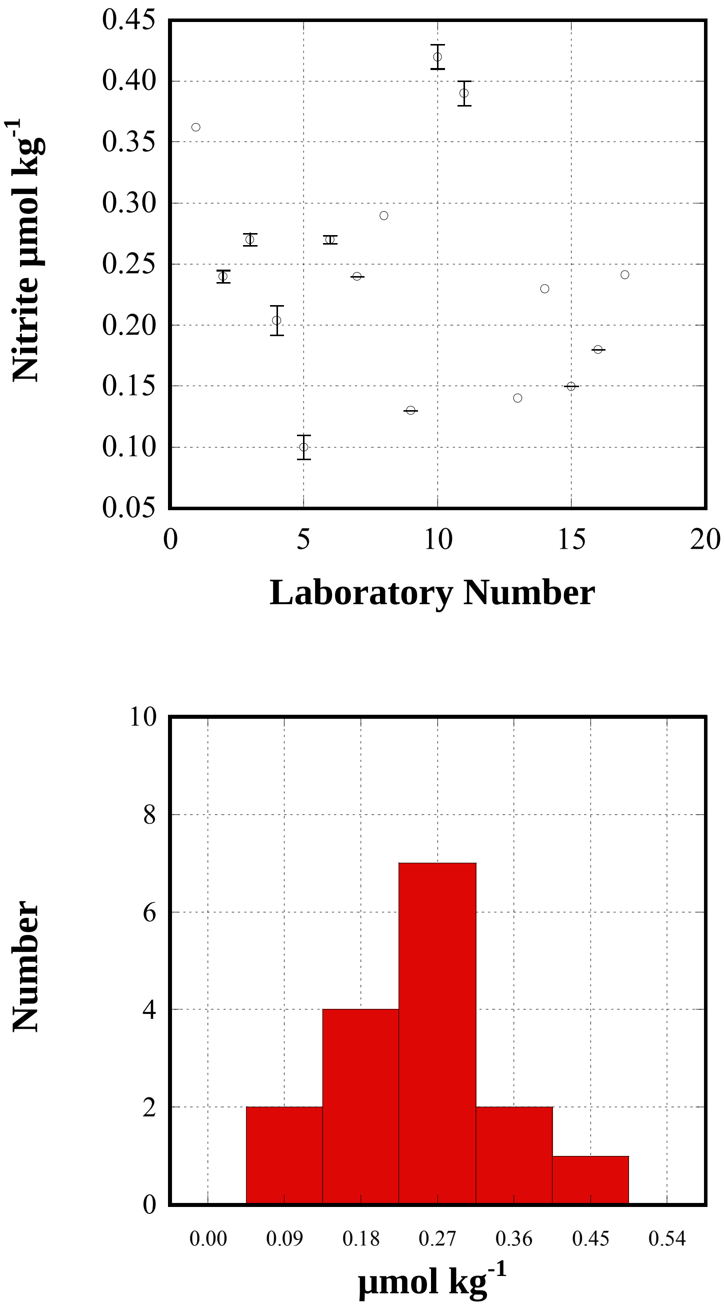


Figure 5-6 Nitrite results for sample 6: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 1 — Nitrate

Consensus Value: 0.04 ± 0.03 µmol kg^{-1}

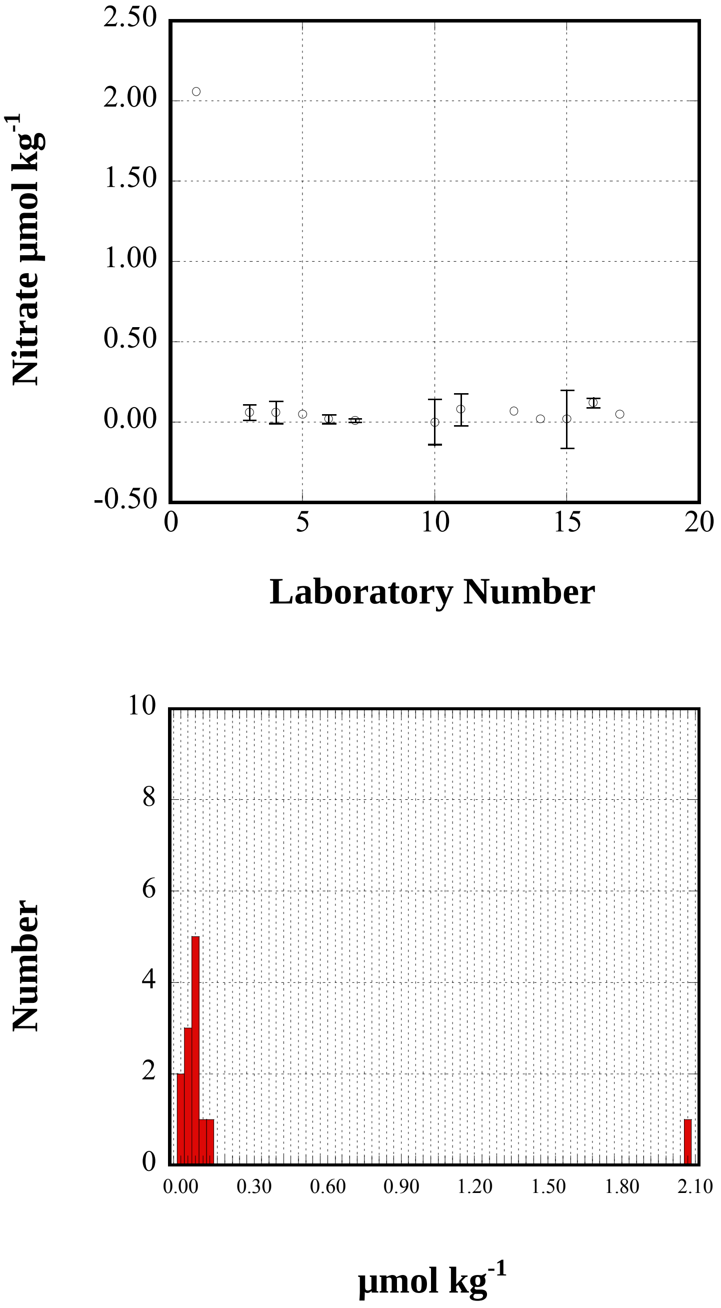
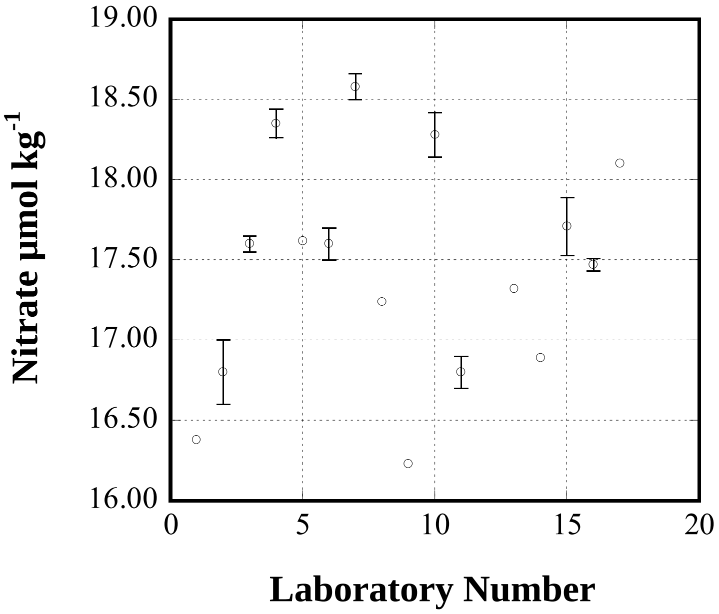


Figure 6-1 Nitrate results for sample 1: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 2 — Nitrate

Consensus Value: 17.4 ± 0.7 µmol kg^{-1}



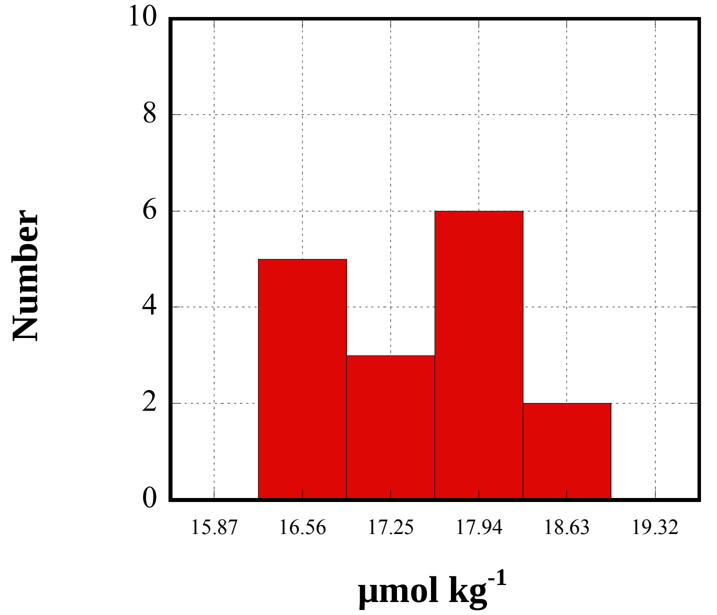
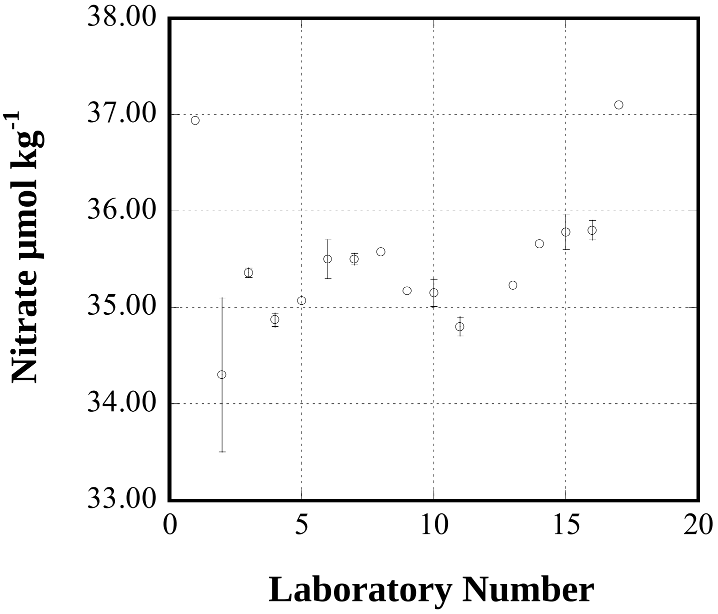


Figure 6-2 Nitrate results for sample 2: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 3 — Nitrate

Consensus Value: 35.3 ± 0.3 µmol kg^{-1}



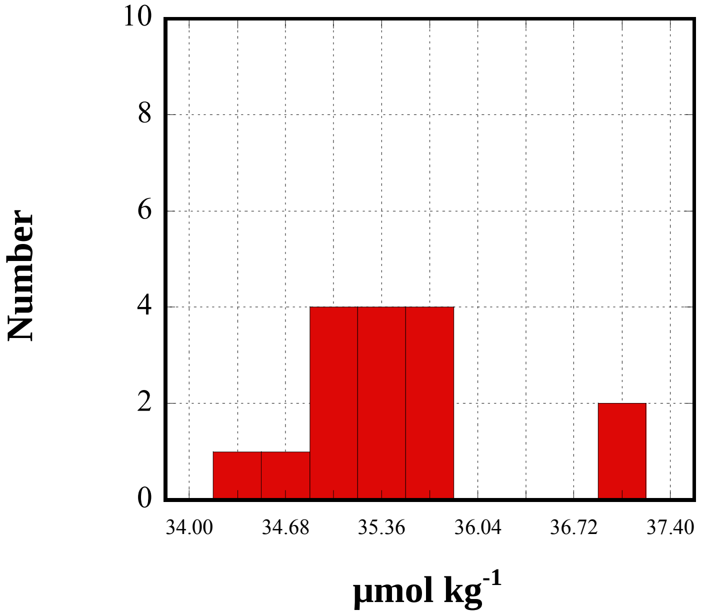


Figure 6-3 Nitrate results for sample 3: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 4 — Nitrate

Consensus Value: 0.02 ± 0.03 µmol kg^{-1}

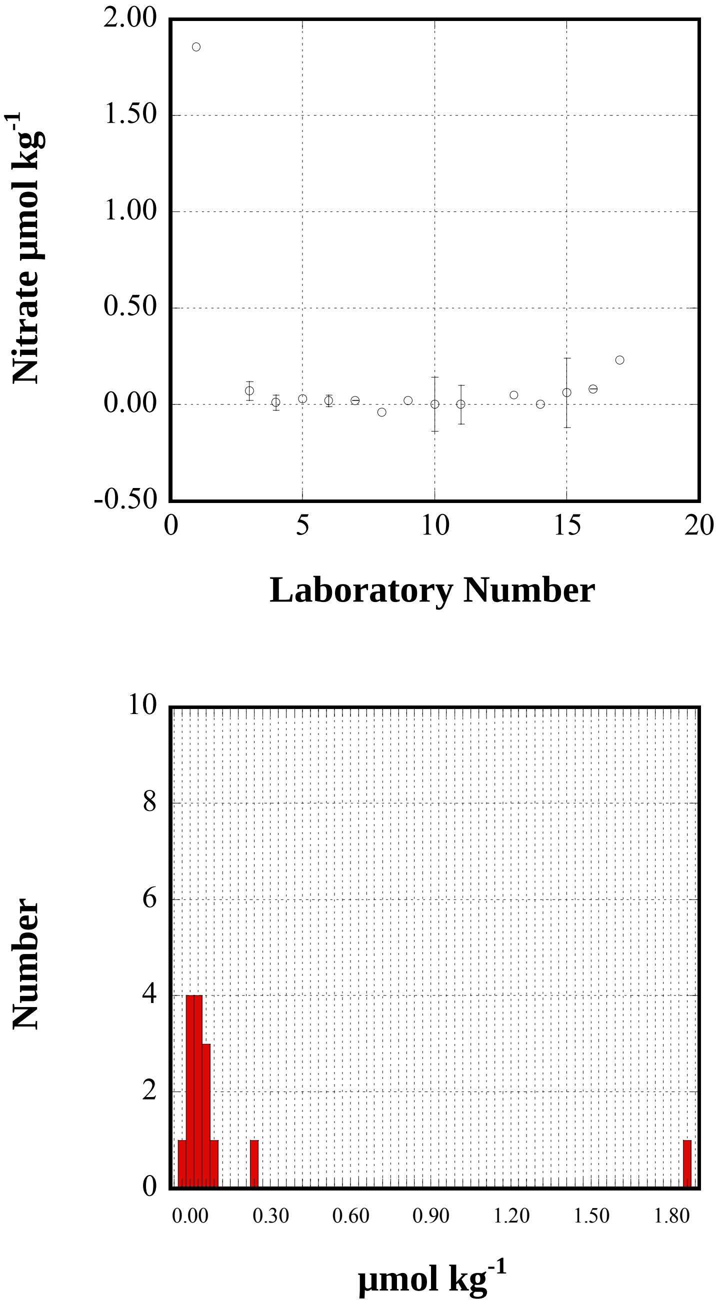


Figure 6-4 Nitrate results for sample 4: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 5 — Nitrate

Consensus Value: 13.1± 0.2 µmol kg^{-1}

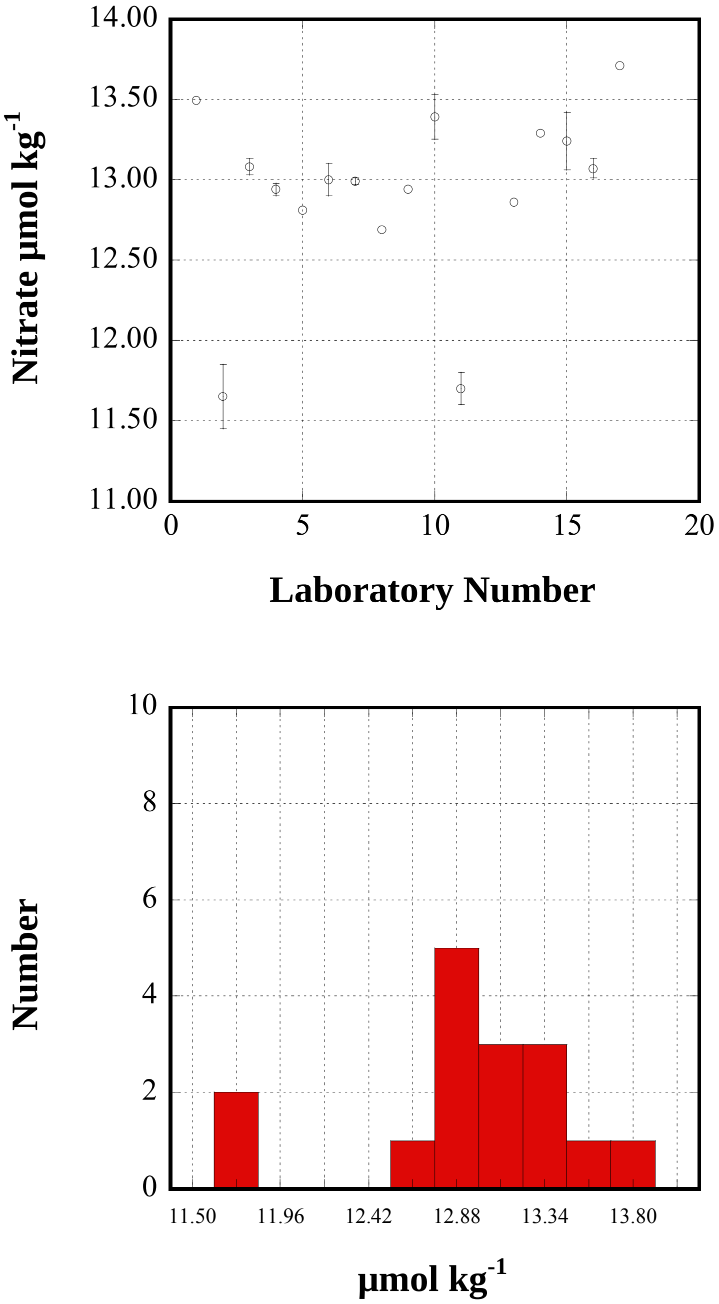


Figure 6-5 Nitrate results for sample 5: concentration *versus* laboratory number (upper panel)

Frequency distribution of concentration (lower panel).

Sample 6 — Nitrate

Consensus Value: 38.2 ± 1.1 µmol kg^{-1}

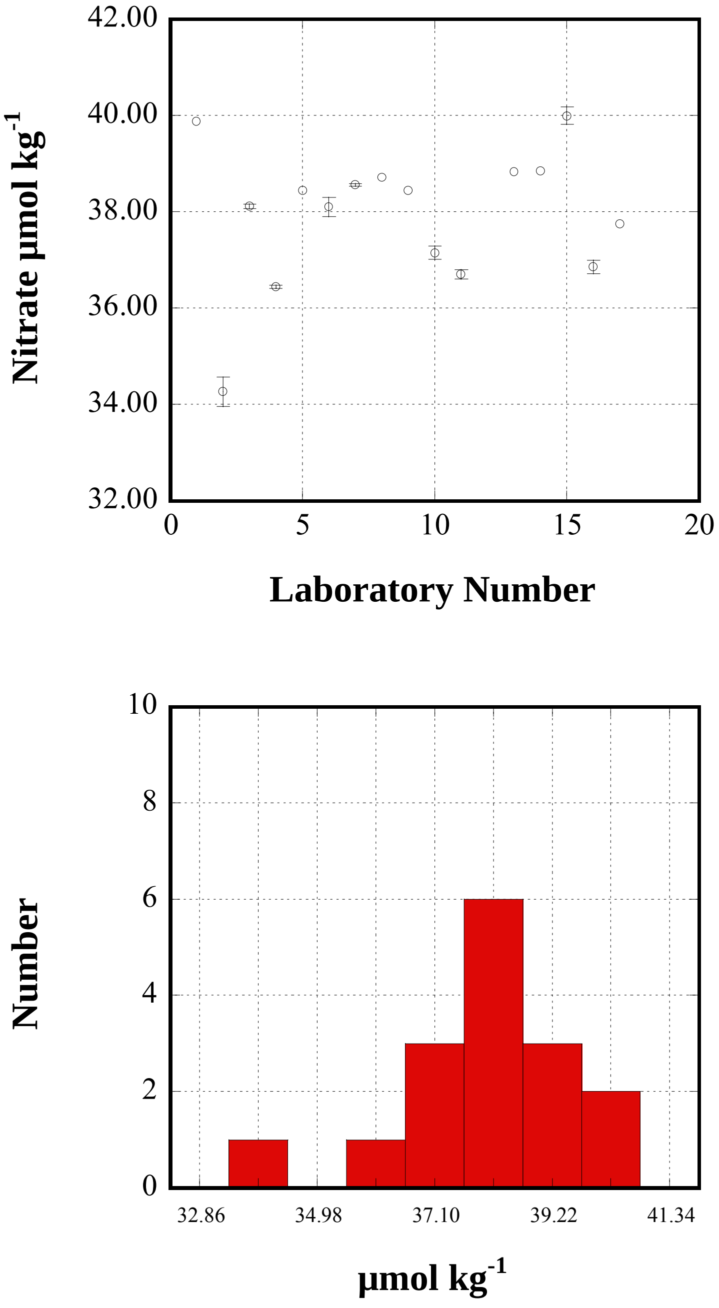


Figure 6-6 Nitrate results for sample 6: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 1 — Nitrate + Nitrite

Consensus Value: 0.06 ± 0.04 µmol kg^{-1}

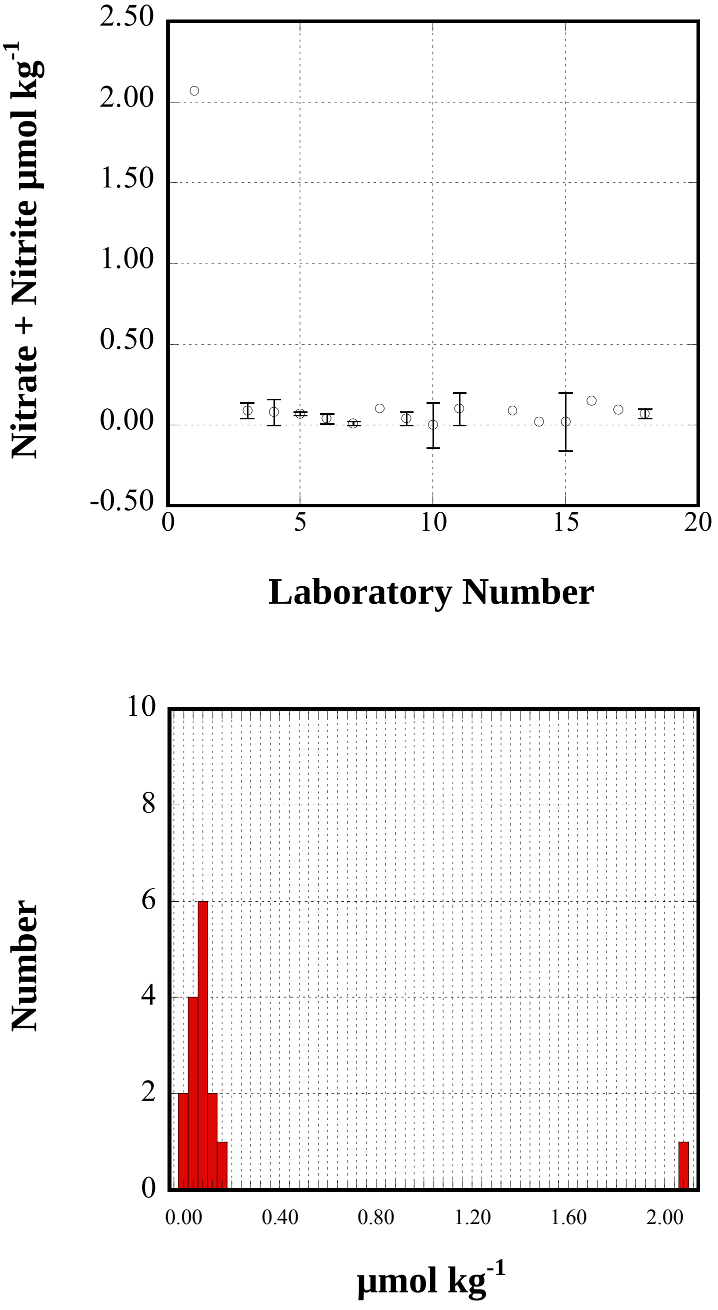
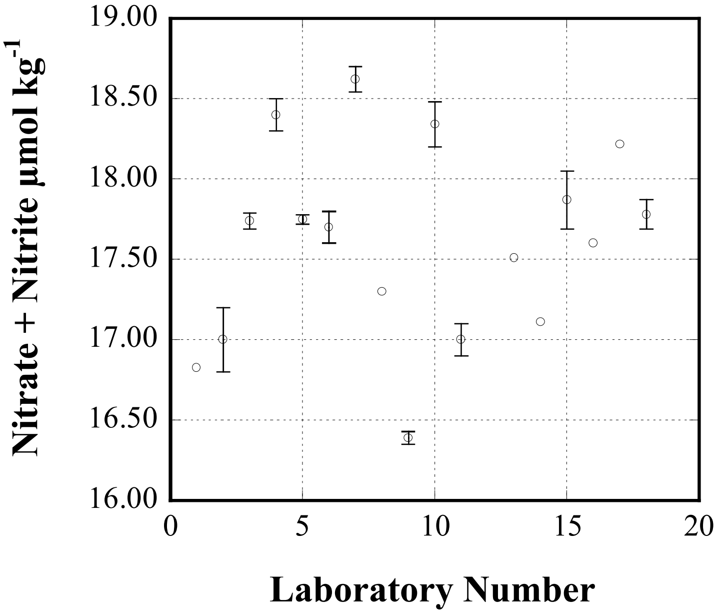


Figure 7-1 Nitrate + nitrite results for sample 1: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 2 — Nitrate + Nitrite

Consensus Value: 17.6 ± 0.6 ? mol kg^{-1}



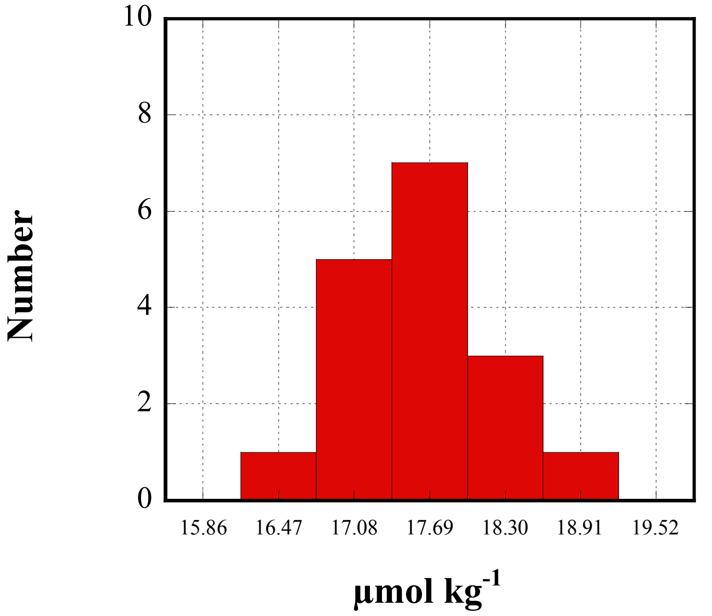
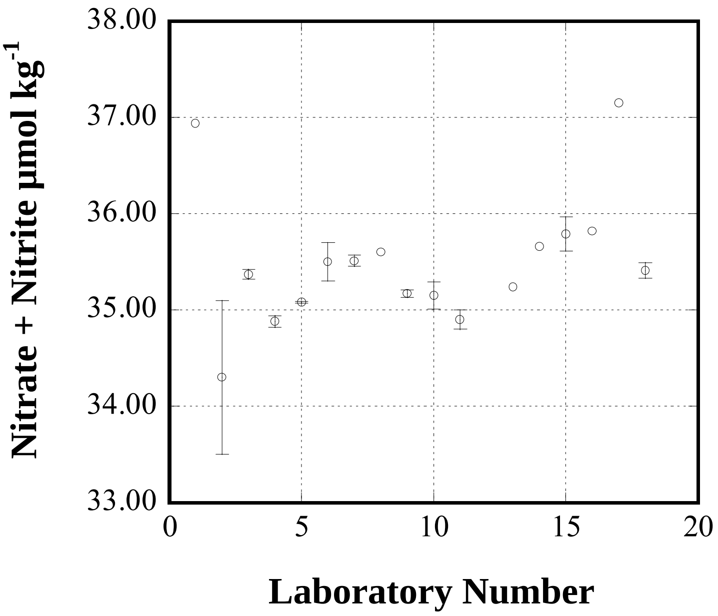


Figure 7-2 Nitrate + nitrite results for sample 2: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 3 — Nitrate + Nitrite

Consensus Value: 35.4 ± 0.3 µmol kg^{-1}



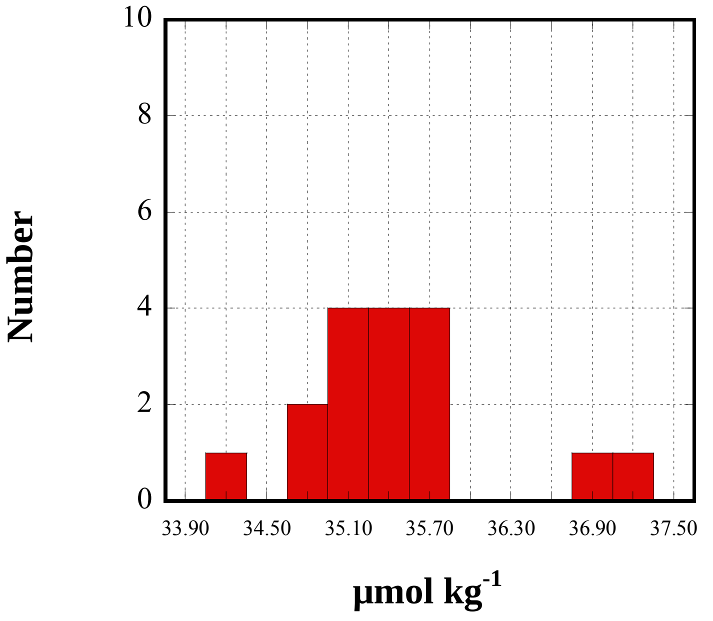
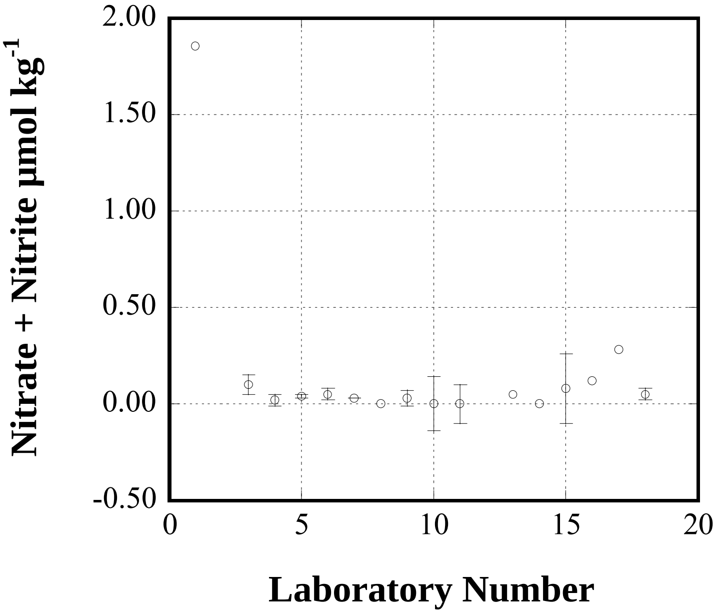


Figure 7-3 Nitrate + nitrite results for sample 3: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 4 — Nitrate + Nitrite

Consensus Value: 0.04 ± 0.04 µmol kg^{-1}



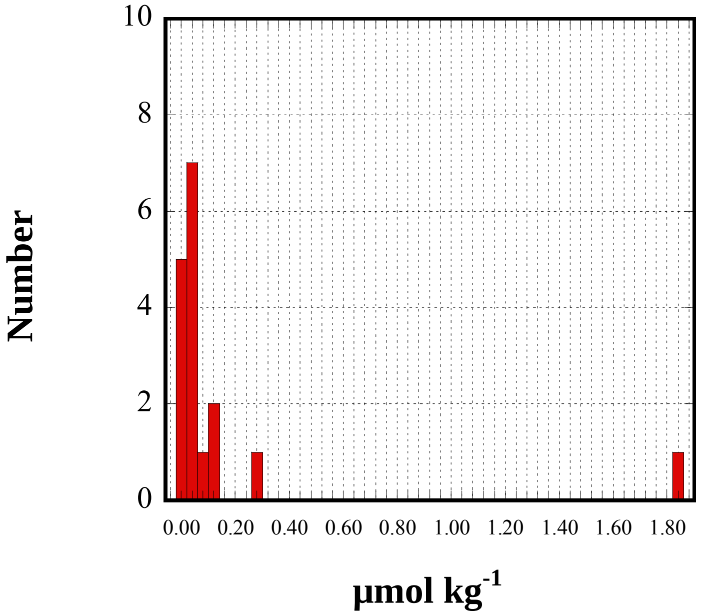


Figure 7-4 Nitrate + nitrite results for sample 4: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 5 — Nitrate + Nitrite

Consensus Value: 14.0 ± 0.2 µmol kg^{-1}

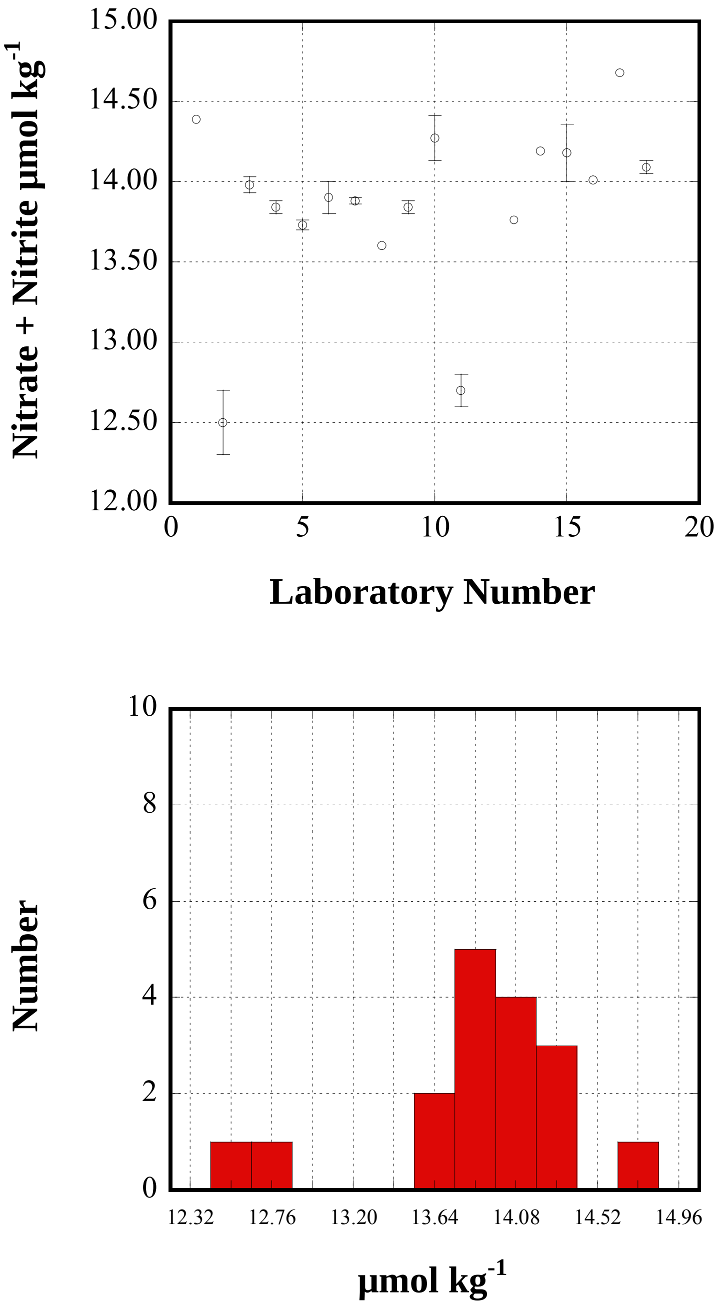
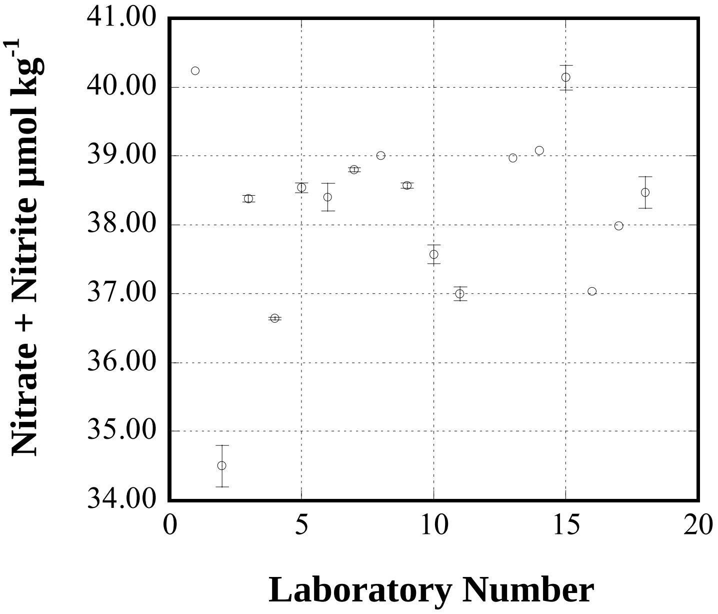


Figure 7-5 Nitrate + nitrite results for sample 5: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 6 — Nitrate + Nitrite

Consensus Value: 38.4 ± 1.0 µmol kg^{-1}



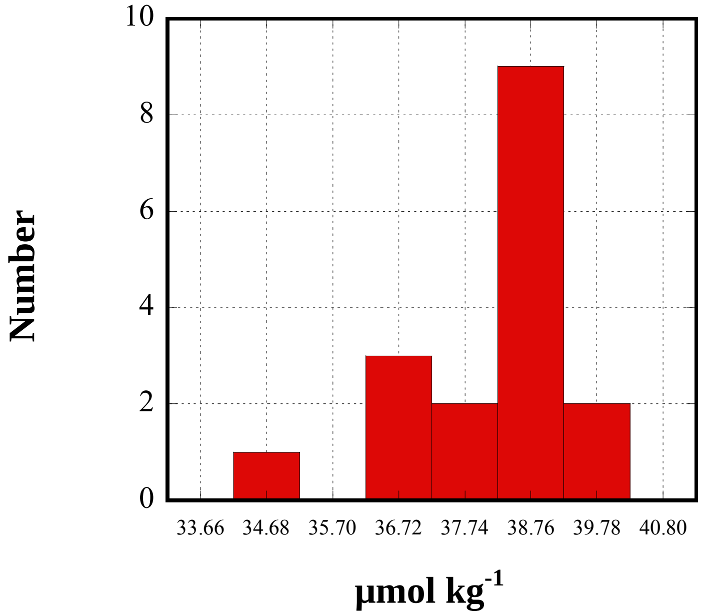


Figure 7-6 Nitrate + nitrite results for sample 6: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 1 — Phosphate

Consensus Value: 0.09 ± 0.02 μmol kg^{-1}

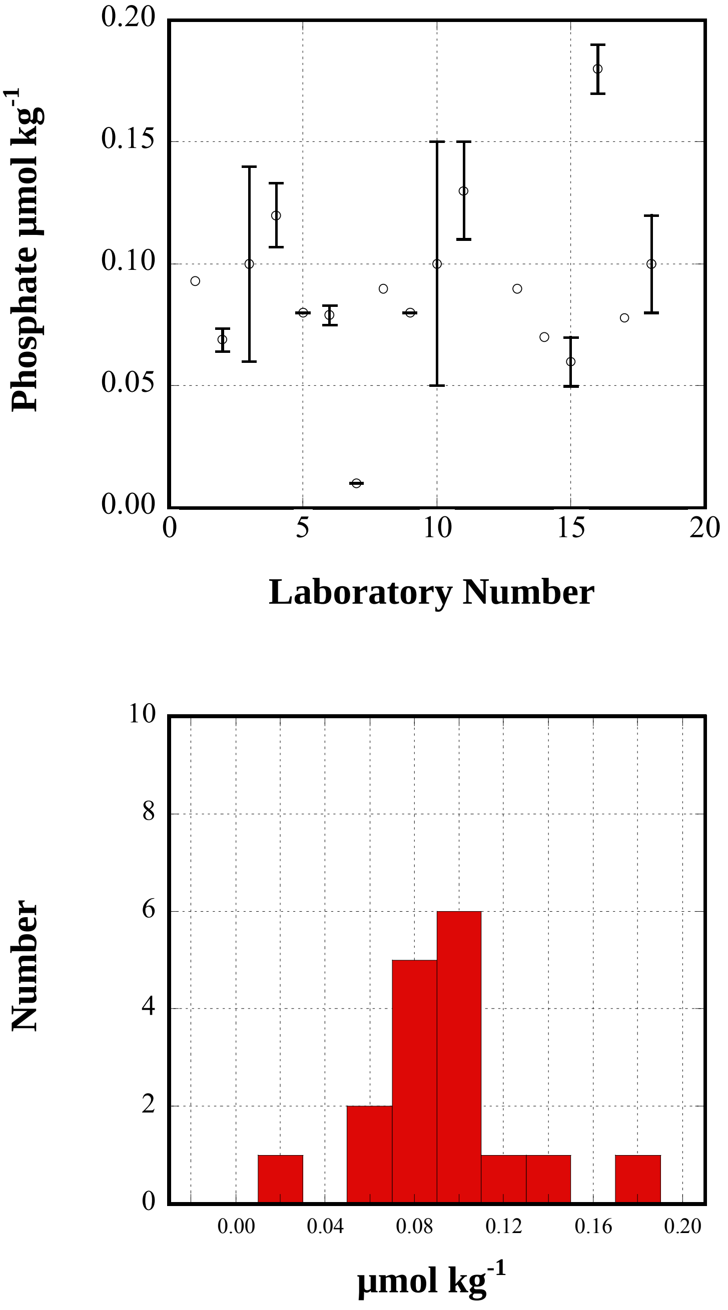


Figure 8-1 Phosphate results for sample 1: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 2 — Phosphate

Consensus Value: 1.25 ± 0.04 µmol kg^{-1}

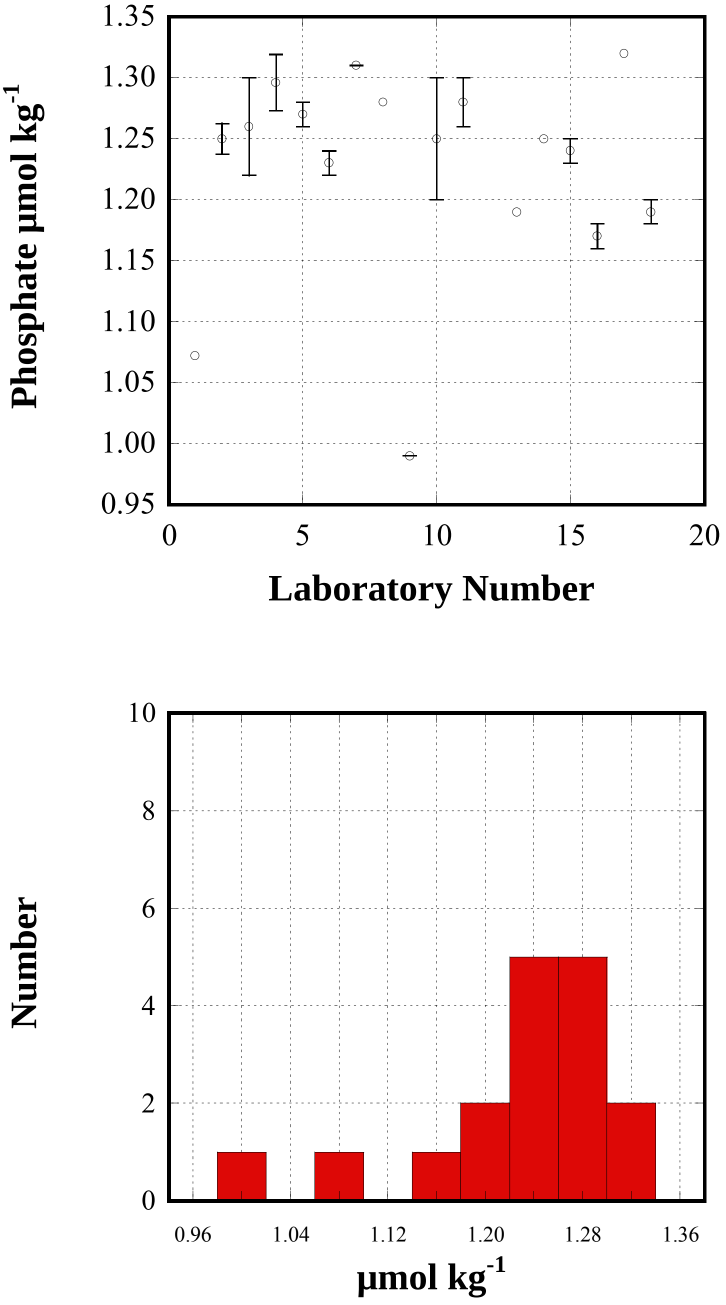


Figure 8-2 Phosphate results for sample 2: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 3 — Phosphate

Consensus Value: 2.14 ± 0.07 µmol kg^{-1}

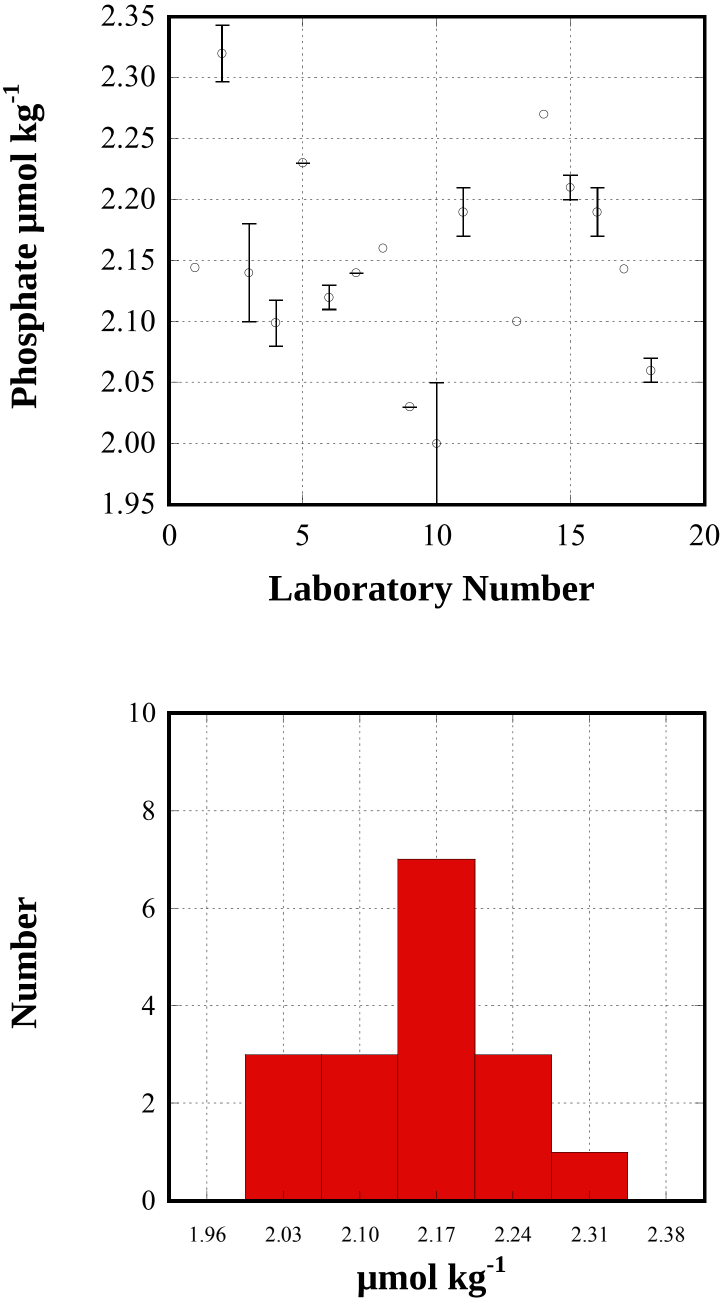
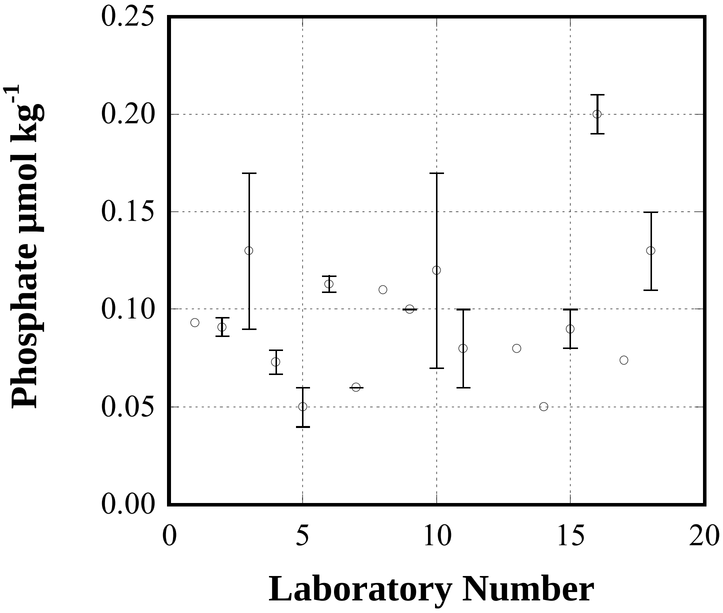


Figure 8-3 Phosphate results for sample 3: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 4 — Phosphate

Consensus Value: 0.09 ± 0.03 µmol kg^{-1}



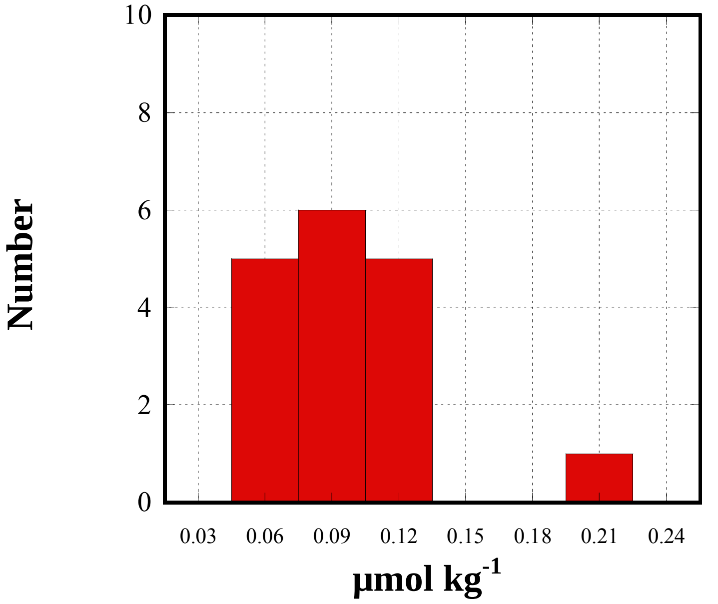
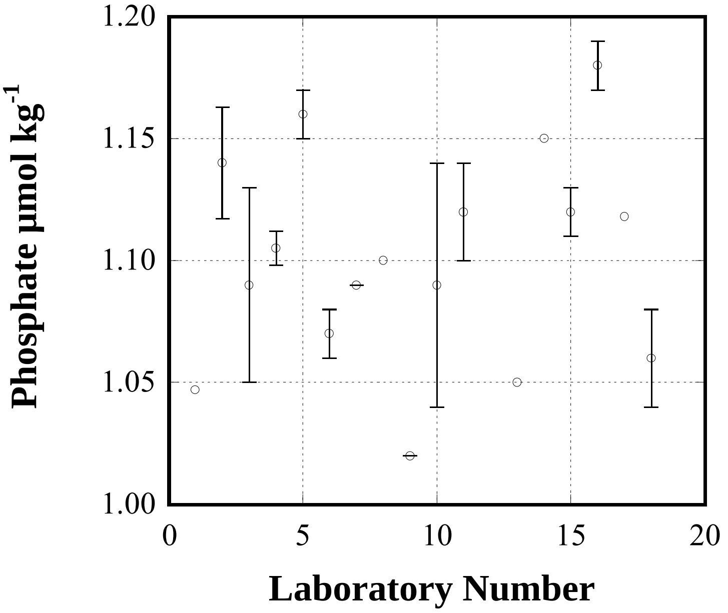


Figure 8-4 Phosphate results for sample 4: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 5 — Phosphate

Consensus Value: 1.10 ± 0.04 µmol kg^{-1}



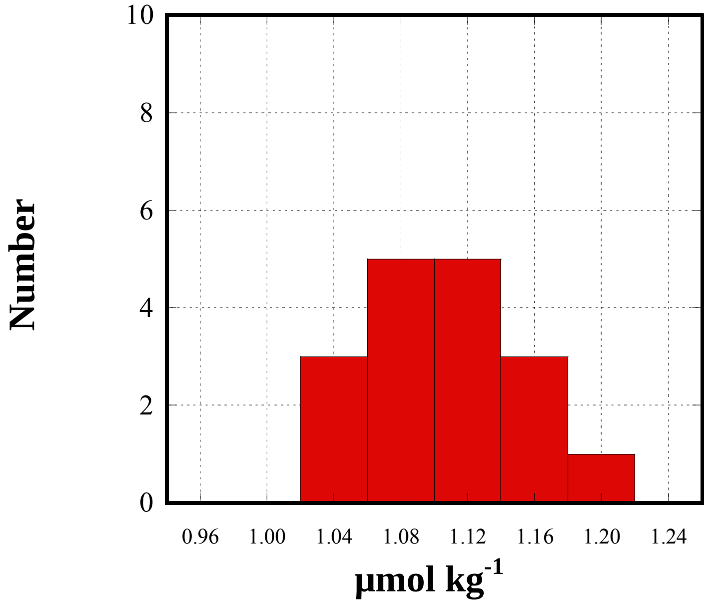
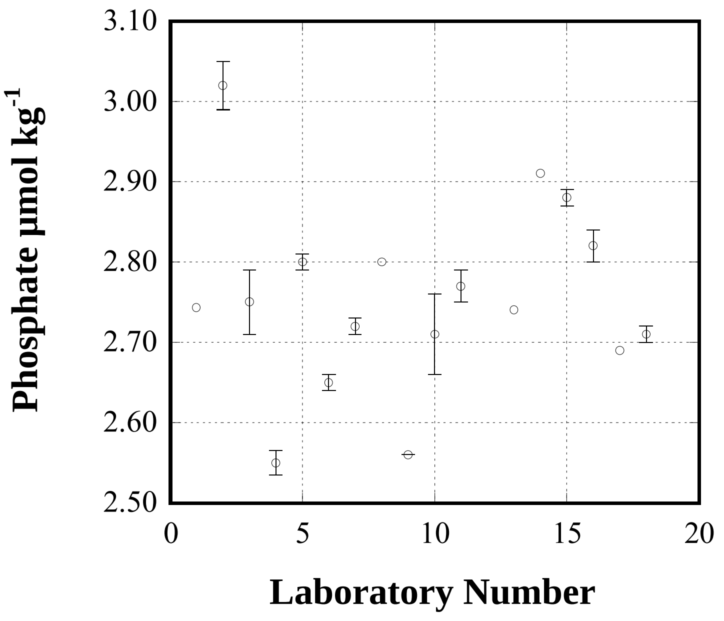


Figure 8-5 Phosphate results for sample 5: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 6 — Phosphate

Consensus Value: 2.74 ± 0.10 µmol kg^{-1}



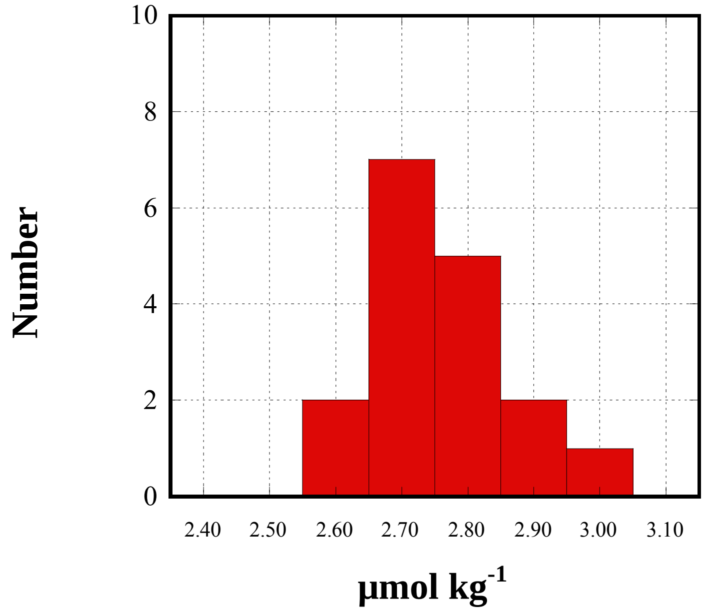


Figure 8-6 Phosphate results for sample 6: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 1 — Silicic acid

Consensus Value: 2.06 ± 0.23 µmol kg^{-1}

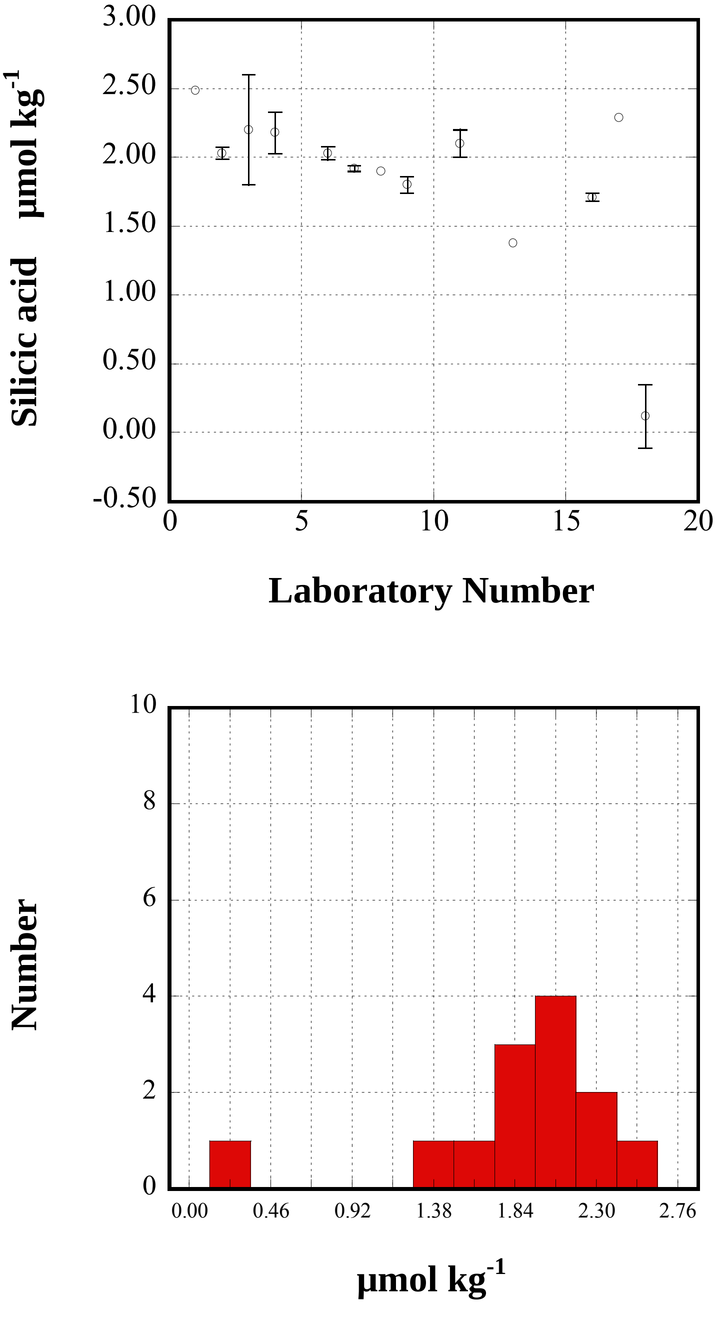


Figure 9-1 Silicic acid results for sample 1: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 2 — Silicic acid

Consensus Value: 66.4 ± 2.0 µmol kg^{-1}

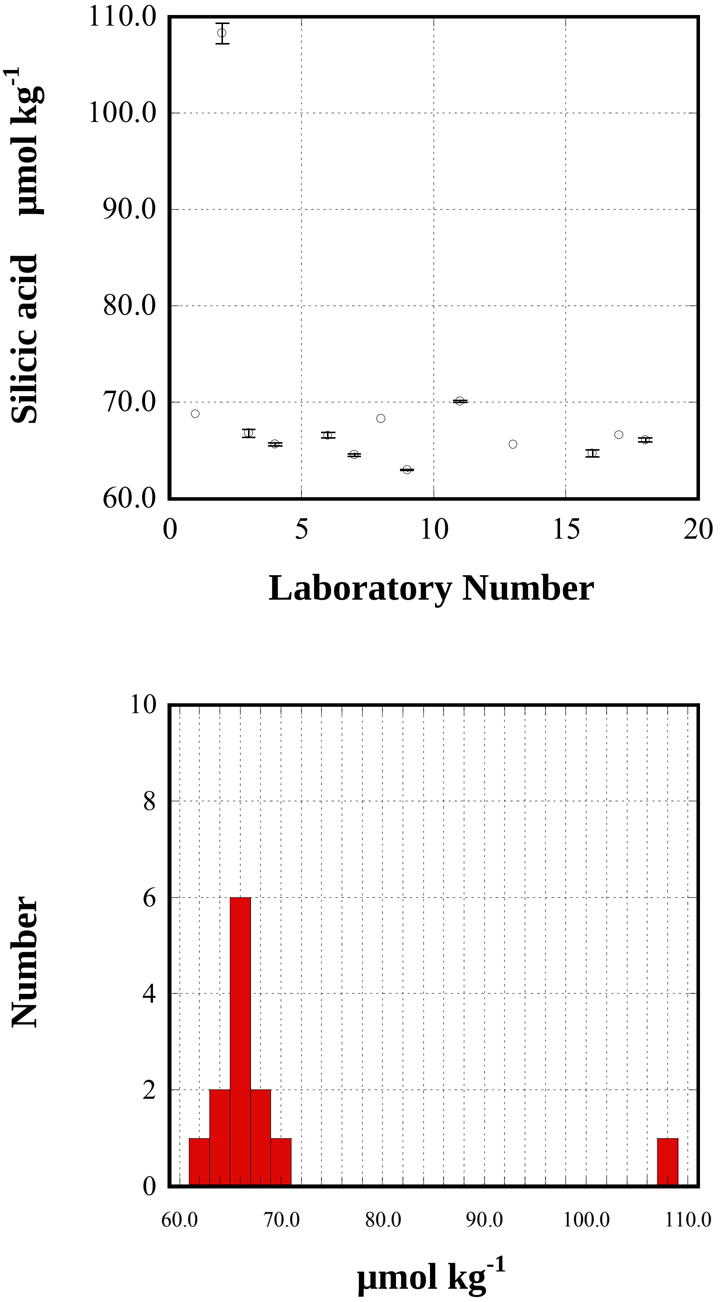


Figure 9-2 Silicic acid results for sample 2: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 3 — Silicic acid

Consensus Value: 135.7 ± 2.3 µmol kg^{-1}

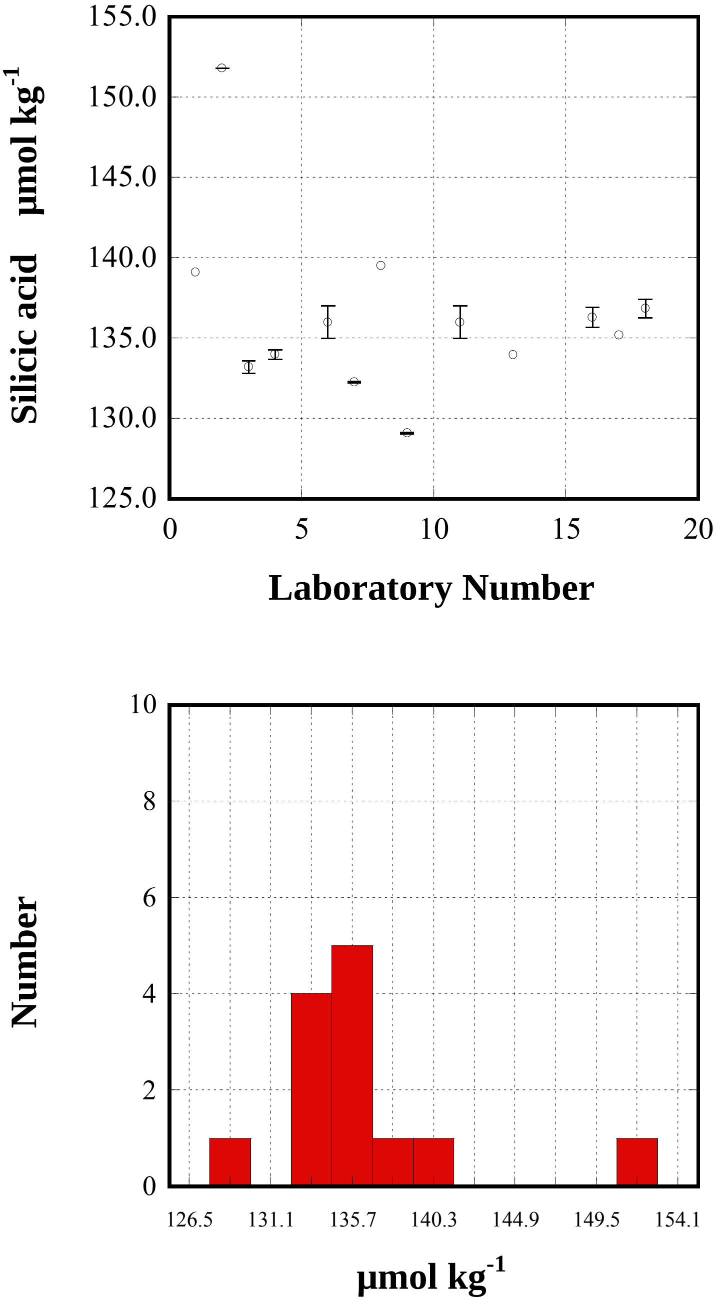


Figure 9-3 Silicic acid results for sample 3: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 4 — Silicic acid

Consensus Value: 2.09 ± 0.31 µmol kg^{-1}

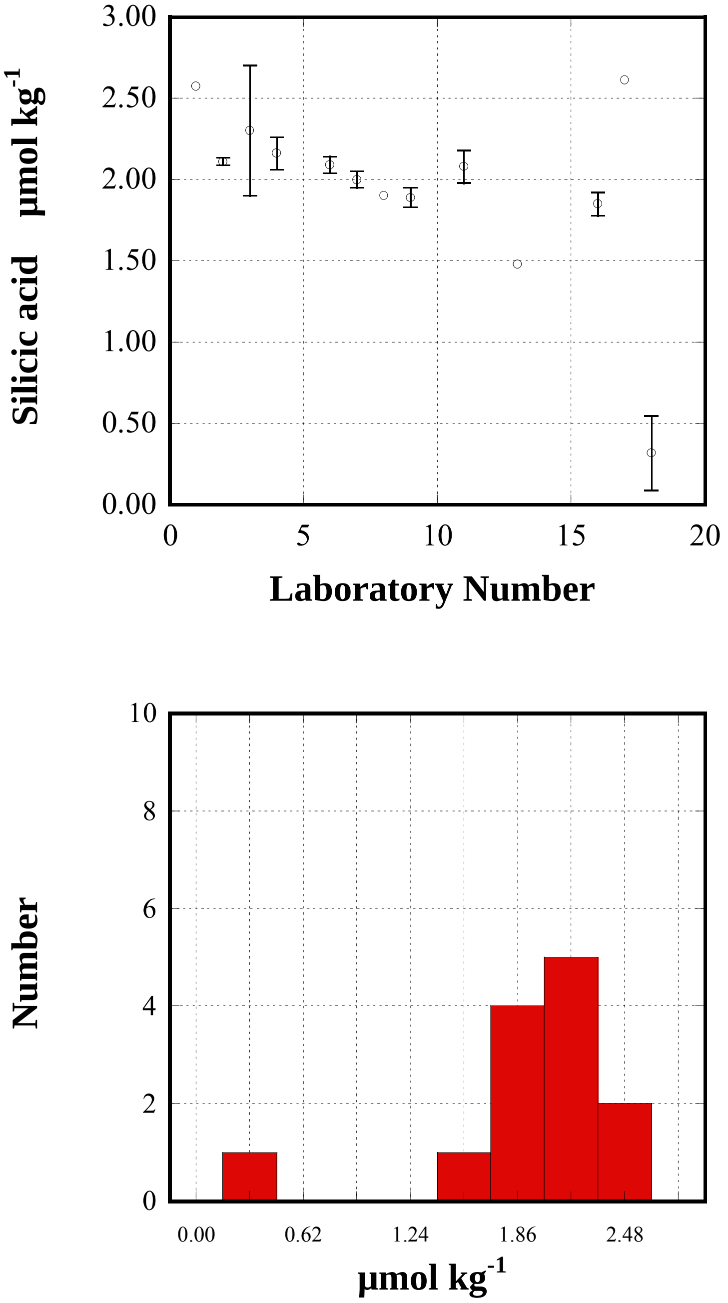


Figure 9-4 Silicic acid results for sample 4: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 5 — Silicic acid

Consensus Value: 73.8 ± 2.4 μmol kg^{-1}

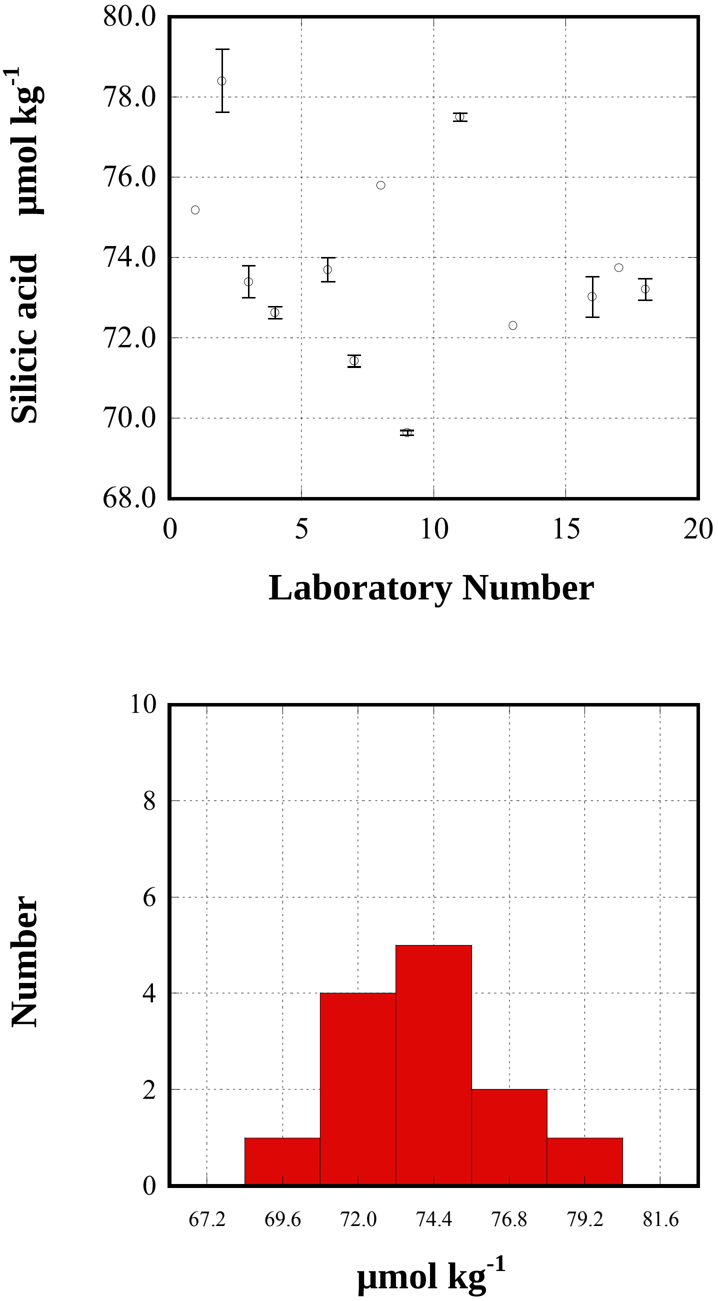
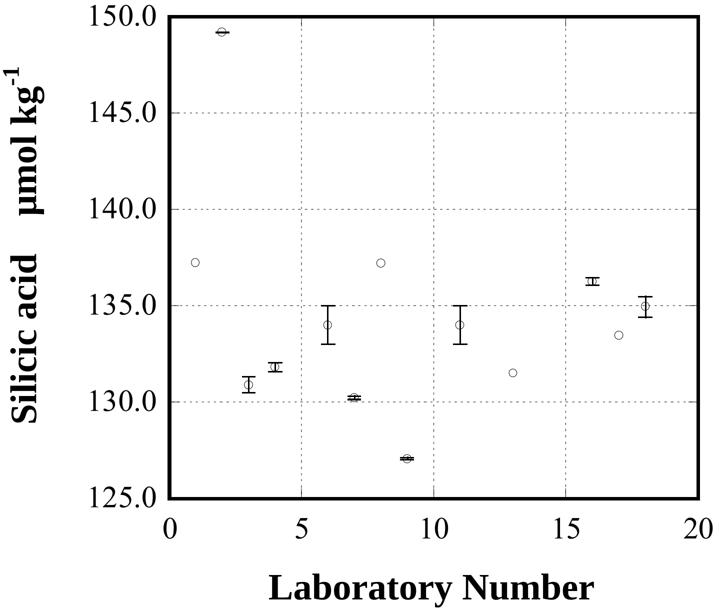


Figure 9-5 Silicic acid results for sample 5: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

Sample 6 — Silicic acid

Consensus Value: 133.8 ±2.5 µmol kg^{-1}



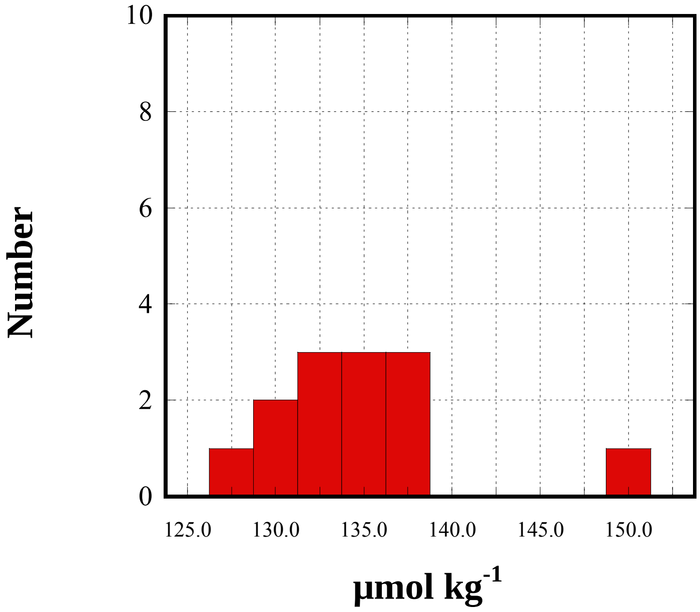


Figure 9-6 Silicic acid results for sample 6: concentration *versus* laboratory number (upper panel)
Frequency distribution of concentration (lower panel).

6. Conclusions

A total of 18 sets of 6 samples each were distributed in 5 countries. Results were returned by 17 laboratories in 5 countries. Although consensus concentrations were obtained for the 6 samples, the standard deviations were 4.5 times and more than 10 times larger than those of the homogeneities for phosphate and silicic acid, respectively. For nitrate, the standard deviations were only about double the homogeneities. These results indicate that variability in in-house standards of the participating laboratories — rather than analytical precision — is the primary source of interlaboratory discrepancy. Therefore use of a certified RMNS is essential for establishing nutrient data sets that can be compared across laboratories, especially for silicic acid and phosphate.

Acknowledgements

The author thanks all participants for their data submission and cooperation throughout this intercomparison exercise. The author also thanks Wenjing Zhu and Mayako Shimizu for data management and preparation of the many graphs and tables in this report.

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Appendix I

List of participating laboratories

Table A1 – List of participating laboratories

Laboratory	Name	Affiliation	Address
1	Minhan DAI	Marine Environmental Laboratory, Xiamen University, China	361005 Xiamen, China
2	Nurit KRESS	Israel Oceanographic and Limnological Research Institute, Israel	P.O. Box 8030, Tel-Shikmona, 31080 Haifa, Israel
3	Doug MASTEN / Susan BECKER	Scripps Institution of Oceanography, STS/ODF, USA	8855 Biological Grade, 215 Isaacs Hall, La Jolla, CA 92037
4	Louis I. GORDON	College of Oceanic and Atmospheric Sciences, Oregon State University, USA	College of Oceanic and Atmospheric Sciences, Oregon State University, 104 Ocean Administration Building, Corvallis, OR 97331-5033
5	Kazuhiro SAITO	Hakodate Marine Observatory, Japan	3-4-4 Mihara, Hakodate-shi, Hokkaido 041-0806, Japan
6	Roger KEROUEL	IFREMER (Centre de Brest)	BP 70, 29280 Plouzane, France
7	Hiroshi OGAWA	Ocean Research Institute, The University of Tokyo, Japan	1-15-1 Minamidai, Nakano-ku, Tokyo 164-8639, Japan
8	Hiroaki SAITO	Tohoku National Fisheries Research Institute, Japan	3-27-5 Shinhama-cho, Shiogama-city, Miyagi 985-0001, Japan
9	Naoki NAGAI	Marine Division, Climate and Marine Department, Japan Meteorological Agency, Japan	1-3-4 Otemachi, Chiyoda-ku, Tokyo 100-8122, Japan
10	Hiroyuki TAKANO	Oceanographical Division, Maizuru Marine Observatory, Japan	901 Shimofukui, Maizuru-city, Kyoto 624-0946, Japan

11	Agnes. YOUENOU	IFREMER DEL/EC/PP	BP 70, 29280 Plouzane, France
13	Akihiko MURATA	Japan Marine Science and Technology Center, Japan	2-15 Natsushima-cho, Yokosuka-city, Kanagawa 237-0061, Japan
14	Hideshi DAIMON	Kobe Marine Observatory, Japan	1-4-3 Wakinohamakaigan-dori, Chuo-ku, Kobe-city, Hyogo 650-0073, Japan
15	Takao SHIMIZU	Nagasaki Marine Observatory, Japan	11-51 Minami-yamate, Nagasaki-city, Nagasaki 850-0931, Japan
16	Hidekazu OTA	KANSO, Japan	3-1-1 Higashikurazi, Katano-city, Osaka 576-0061, Japan
17	Atsushi TSUDA / Hiromi KASAI	Hokkaido National Fisheries Research Institute	116 Katsurakoi, Kushiro, Hokkaido 085-0802, Japan
18	Katsumi YOKOUCHI	Seikai National Fisheries Research Institute	3-30 Kokubu-machi, Nagasaki 850-0951, Japan

Appendix II

Results submitted by participating laboratories

Laboratory 1

Report on Nutrient Intercomparison Results

April 29, 2003

LABORATORY: Ocean Carbon Group, Marine Environmental Laboratory, Xiamen University, Xiamen, China
Contact: Minhan Dai, mdai@xmu.edu.cn

DATE OF RECEIPT OF SAMPLE: Jan. 18, 2003

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid	Remarks
Sample 1	0.012	2.057	2.069	0.093	2.486	Shortage of volume
Sample 2	0.448	16.379	16.827	1.072	68.793	
Sample 3	ND*	36.936	36.936	2.144	139.093	
Sample 4	ND*	1.855	1.855	0.093	2.572	Shortage of volume
Sample 5	0.896	13.491	14.387	1.047	75.186	
Sample 6	0.362	39.872	40.233	2.743	137.229	

Unit: mol kg^{-1}
* Under detection limit

BRIEF DESCRIPTIONS OF ANALYSIS:
Nitrite (NO_2), phosphate (PO_4), and silicic acid (H_2SiO_3) were determined colorimetrically using a flow injection analyzer (Tri-223 autoanalyzer). Nitrate (NO_3) plus NO_2 was measured by reducing nitrate to nitrite using the same Tri-223 autoanalyzer with an on-line Cd coil.

COMMENTS;

1. **Analysis date**: April 28, 2003
2. We experienced a shortage of samples during the runs for samples 1 and 4.
3. Concentration units have been converted from µmol L^{-1} to µmol kg^{-1} according to Millero (1996) (*Chemical Oceanography*, 2nd edition).
4. We'd like to know more about the preparation procedure of the samples that were provided for this intercomparison exercise. We are concerned about the way the samples were stored.

Laboratory 2

Dr. Michio Aoyama
Geochemical Res. Dept.
Meteorological Res. Inst.
1-1 Nagamina, Tsukuba
305-0052, Japan

30 April 2003

Re: 2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

Dear Michio,

Below are the results of the analysis we performed on the six samples sent to us by the Marine Chemistry Department of the Israel Oceanographic and Limnological Research Institute, P.O. Box 8030, Tel-Shikmona, 31080 Haifa, Israel

The samples arrived in good shape on January 2003 and were analyzed on April 28, 2003. They were kept refrigerated during the whole time.

Comments:

1. Because we usually run samples with very low concentrations, samples 2, 3, 5, and 6 were diluted before analysis with low-nutrient seawater from the eastern Mediterranean
2. Samples 1 and 4 were run without dilution.
3. Triplicate samples were run and the average computed
4. Bdl – The detection limit for nitrate + nitrite and nitrite is 0.08 micromolar.
5. The concentrations in micromoles per liter were transformed to micromoles per kilogram using the density calculated from the given salinity and the temperature of the sample during analysis

Looking forward to the results of the intercomparison.

Sincerely,

Dr. Nurit Kress

Table of results in micromoles per liter

Sample		$NO_3 + NO_2$	NO_2	PO_4	$Si(OH)_4$	Salinity	Temp.	Density
		Micromoles per liter						
S1	**average**	**Bdl**	**Bdl**	**0.071**	**2.08**	34.75	20	1.02457
	std. dev.			0.005	0.04			
	CV (%)			7	2			
S2	**average**	**17.4**	**0.20**	**1.28**	**110.9**	34.65	20	1.0245
	std. dev.	0.2	0.00	0.02	0.7			
	CV (%)	1	0	1	1			
S3	**average**	**35.1**	**Bdl**	**2.38**	**155.5**	34.65	20	1.0245
	std. dev.	0.8		0.02	0.4			
	CV (%)	2		1	0			
S4	**average**	**Bdl**	**Bdl**	**0.094**	**2.16**	34.8	20	1.02461
	std. dev.			0.005	0.03			
	CV (%)			5	1			
S5	**average**	**12.8**	**0.87**	**1.17**	**80.3**	34.6	20	1.02446
	std. dev.	0.2	0.03	0.02	0.9			
	CV (%)	2	4	2	1			
S6	**average**	**35.3**	**0.25**	**3.09**	**152.9**	34.5	20	1.02438
	std. dev.	0.3	0.01	0.02	0.2			
	CV (%)	1	2	1	0			

Table of results in micromoles per kilogram

Sample		$NO_3 + NO_2$	NO_2	PO_4	$Si(OH)_4$
		Micromoles per kilogram			
S1	**Average**	**Bdl**	**Bdl**	**0.069**	**2.03**
S2	**Average**	**17.0**	**0.20**	**1.25**	**108.3**
S3	**Average**	**34.3**	**Bdl**	**2.32**	**151.8**
S4	**Average**	**Bdl**	**Bdl**	**0.091**	**2.11**
S5	**Average**	**12.5**	**0.85**	**1.14**	**78.4**
S6	**Average**	**34.5**	**0.24**	**3.02**	**149.2**

A brief description of the methods used:

The nutrients were analyzed on a SAN^{plus} System autoanalyzer (Skalar, Breda, The Netherlands) equipped with an automatic SA 1000 sampler, three colorimeters, and a data acquisition module with FlowAccess® software (Windows software for Skalar SAN^{plus} systems). The peristaltic pump and the cartridges were from Bran+Luebbe.

The chemistries are as follows:
NO_3 + NO_2 — Nitrate is reduced to nitrite under alkaline conditions in a copperized cadmium reductor coil. The nitrite reduced from nitrate, plus any free nitrite already present, reacts under acidic conditions with sulphanilamide to form a diazo compound, which then couples with *N*-1-naphthyl-ethylenediamine dihydrochloride to form a reddish-purple azo dye, which is measured at 520 nm.

$Si(OH)_4$ — Silicic acid reacts with ammonium molybdate in an acidic medium to form silicomolybdic acid which is reduced to molybdenum blue with stannous chloride. The absorption of the colored complex is measured at 630 nm.

PO_4 — Phosphate reacts with ammonium molybdate in an acidic medium to form a phosphomolybdic acid, which is in turn reduced to phosphomolybdous acid by hydrazine sulfate. The intensity of the blue color of the latter compound is measured at 880 nm.

If you need any more information about the methods please let me know.

Laboratory 3

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY:
Scripps Institution of Oceanography
STS/ODF

DATE OF RECEIPT OF SAMPLES:
13 Jan 2003

DATA OF ANALYSIS:
All samples analyzed on 15 Jan 2003

Results in micromoles per kilogram = micromoles per liter/density

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.03	0.06	0.09	0.10	2.2
Sample 2	0.14	17.60	17.74	1.26	66.8
Sample 3	0.01	35.36	35.37	2.14	133.2
Sample 4	0.03	0.07	0.10	0.13	2.3
Sample 5	0.90	13.08	13.98	1.09	73.4
Sample 6	0.27	38.11	38.38	2.7	130.9

Estimation of analytical error:

NO_2	±0.005
$NO_3 + NO_2$	±0.05
PO_4	±0.04
SiO_3	±0.40

Brief description of analyses:

Samples were analyzed with a modified Technicon AAII.

1. A modification of the Armstrong et al. (1967) procedure was used for the analysis of nitrate + nitrite and nitrite. Nitrate is quantitatively reduced to nitrite by passing the

sample through a Cd/Cu reduction column. The sample is then passed through a 15-mm flowcell and absorbance measured at 540 nm.

2. Orthophosphate was analyzed using a modification of the Bernhardt and Wilhelms (1967) method using dihydrazine sulfate as a reductant of the sample in an acidified ammonium molybdate solution. The sample was passed through a 50-mm flowcell and absorbance measured at 820 nm.

3. Silicic acid was analyzed using a modification of the Armstrong et al. (1967) method. Stannous chloride was used as a reductant of the sample in an acidified ammonium molybdate solution. Tartaric acid was added to eliminate PO_4 interference. The sample was passed through a 15-mm flowcell and absorbance measured at 660 nm.

References:

Armstrong, F.A.J., C.R. Stearns and J.D.H. Strickland. 1967. The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment. Deep-Sea Research 14(3):381–389.

Bernhardt, H. and A. Wilhelms. 1967. The continuous determination of low level iron, soluble phosphate and total phosphate with the AutoAnalyzer. Technicon Symposium, 1967, Vol. I, p. 386.

Laboratory 4

Results for 2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY:
College of Oceanic and Atmospheric Sciences, Oregon State University

DATE OF RECEIPT OF SAMPLES:
13-Jan-03

DATE OF ANALYSIS:
13-Jan-03 All samples

Results in micromoles per kilogram

	Nitrite		Nitrate		Nitrate + nitrite		Phosphate		Silicic acid		
	Mean	±	**Mean**	±	**Mean**	±	**Mean**	±	**Mean**	±	***N***
Sample 1	0.023	0.007	0.06	0.07	0.08	0.08	0.120	0.013	2.18	0.15	4
Sample 2	0.044	0.007	18.35	0.09	18.40	0.10	1.296	0.023	65.64	0.17	4
Sample 3	0.014	0.005	34.87	0.07	34.88	0.06	2.099	0.019	134.00	0.29	5
Sample 4	0.010	0.009	0.01	0.04	0.02	0.03	0.073	0.006	2.16	0.10	4
Sample 5	0.893	0.011	12.94	0.04	13.84	0.04	1.105	0.007	72.63	0.15	4
Sample 6	0.204	0.012	36.44	0.03	36.64	0.02	2.550	0.015	131.82	0.24	4

± = 95% confidence level

Brief descriptions of analysis:

All four nutrients were analyzed simultaneously on a hybrid autoanalyzer consisting of a Technicon AAII for the determination of phosphate and an ALPKEM RFA 300 for the determination of silicic acid, nitrite, and nitrate + nitrite.

A description of the chemistries can be found in:
A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study.

WOCE Hydrographic Program Office, WHP Office Report WHPO 91-1, Part 3.1.3: WHP Operations and Methods, WOCE Report No. 68/91, November 1994.

Comments:

Samples were in good shape prior to analysis and no problems occurred during the single run.
Prior to the analysis on March 19th, the samples were stored in the dark at room temperature.

Laboratory 5

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY:
KOHUMARU (HAKODATE)

DATE OF RECEIPT OF SAMPLES:
2003/1/16 (Japan Standard Time)

DATE OF ANALYSIS:		
	Sample 1	2003/2/20 17:22 (JST)
	Sample 2	2003/2/20 17:22 (JST)
	Sample 3	2003/2/20 17:22 (JST)
	Sample 4	2003/2/20 17:22 (JST)
	Sample 5	2003/2/20 17:22 (JST)
	Sample 6	2003/2/20 17:22 (JST)

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.02 ± 0.00	0.05	0.07 ± 0.01	0.08 ± 0.00	—
Sample 2	0.13 ± 0.01	17.62	17.75 ± 0.03	1.27 ± 0.01	—
Sample 3	0.01 ± 0.00	35.07	35.08 ± 0.01	2.23 ± 0.00	—
Sample 4	0.01 ± 0.00	0.03	0.04 ± 0.01	0.05 ± 0.01	—
Sample 5	0.92 ± 0.00	12.81	13.73 ± 0.03	1.16 ± 0.01	—
Sample 6	0.10 ± 0.01	38.44	38.54 ± 0.07	2.80 ± 0.01	—

Brief descriptions of the methods of analysis:

Measurements were performed with an AutoAnalyzer^{TM}-II (Technicon^{TM}). Distilled water was tightly sealed in clean bottles and opened just before use for zero-base. PO_4 measurements were based upon the method of Murphy and Riley (1961). NO_2 and NO_3 were measured in accordance with the technique of Armstorng et al. (1967), and NO_3 concentrations were calculated by subtracting NO_2 from NO_3 + NO_2. Since calibration curves of PO_4 and NO_3 were not linear at low concentrations, we applied quadratic calibration curves.

Order of standard and RMNS was as follows:

0, 1/4, 2/4, 3/4, 4/4, 3/4, 2/4, 1/4, 0, ← standard for linearity check
RMNS-1, RMNS-1, RMNS-1, RMNS-1,
RMNS-2, RMNS-2, RMNS-2, RMNS-2,
…………
RMNS-6, RMNS-6, RMNS-6, RMNS-6

Comments

No baseline drift occurred through the measurement. Peak shapes were neat enough.

We could not measure salinity values of RMNS because their remainders were too small. Conversion of concentrations (from μmol L^{-1} to μmol kg^{-1}) was carried out using the given salinity values.

Laboratory 6

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY:

R. KEROUEL
IFREMER, Centre de Brest
Département DEL/EC/EB
BP 70, 29280 Plouzane
France

DATE OF RECEIPT OF SAMPLES: 14 JAN 2003

DATA OF ANALYSIS:	Sample 1	N & P: 23/01/03; Si: 27/01/03
	Sample 2	N & P: 23/01/03; Si: 27/01/03
	Sample 3	N & P: 23/01/03; Si: 27/01/03
	Sample 4	N & P: 23/01/03; Si: 27/01/03
	Sample 5	N & P: 23/01/03; Si: 27/01/03
	Sample 6	N & P: 23/01/03; Si: 27/01/03

Note: after N & P analysis, the samples were immediately recapped and placed in a refrigerator until Si analysis.

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	**0.023** ± 0.003	**0.02** ± 0.03	**0.04** ± 0.03	**0.079** ± 0.004	**2.03** ± 0.05
Sample 2	**0.150** ± 0.003	**17.6** ± 0.1	**17.7** ± 0.1	**1.23** ± 0.01	**66.6** ± 0.3
Sample 3	**0.012** ± 0.003	**35.5** ± 0.2	**35.5** ± 0.2	**2.12** ± 0.01	**136** ± 1
Sample 4	**0.033** ± 0.003	**0.02** ± 0.03	**0.05** ± 0.03	**0.113** ± 0.004	**2.09** ± 0.05
Sample 5	**0.918** ± 0.005	**13.0** ± 0.1	**13.9** ± 0.1	**1.07** ± 0.01	**73.7** ± 0.3
Sample 6	**0.270** ± 0.003	**38.1** ± 0.2	**38.4** ± 0.2	**2.65** ± 0.01	**134** ± 1

Brief descriptions of analysis: automated analysis. Bran+Luebbe Autoanalyzer AA3 for nitrate and nitrite. Technicon Autoanalyzer AA2 for phosphate and silicic acid. Methods proposed by Tréguer and Le Corre (1975) with only minor modifications.

Tréguer, P. and Le Corre, P., 1975. Manuel d'analyse des sels nutritifs dans l'eau de mer. LOC-UBO, Brest, 110 pp.

Your comments: none

Laboratory 7

Results for RMNS

Unit; µmol kg^{-1}

	Nitrite		Nitrate		Nitrite + nitrate		Phosphate		Silicic acid	
Sample	Ave	±SD	Ave	±SD	Ave	±SD	Ave	±SD	Ave	±SD
1	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	1.92	0.02
2	0.04	0.00	18.58	0.08	18.62	0.08	1.31	0.00	64.55	0.14
3	0.01	0.00	35.50	0.06	35.51	0.06	2.14	0.00	132.27	0.05
4	0.01	0.00	0.02	0.00	0.03	0.00	0.06	0.00	2.00	0.05
5	0.90	0.00	12.99	0.02	13.88	0.02	1.09	0.00	71.42	0.14
6	0.24	0.00	38.56	0.03	38.80	0.03	2.72	0.01	130.23	0.08

Analysis date: Apr 11, 2003

Analysts: Hiroshi Ogawa and Yoko Fujimoto, Ocean Research Institute, The University of Tokyo

Instrument: AACS III, BRAN+LUEBBE Co.

* Triplicate analyses for each sample

Laboratory 8

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY: Tohoku National Fisheries Research Institute, Fisheries Research Agency

DATE OF RECEIPT OF SAMPLES:
Jan 2003

DATA OF ANALYSIS:

Sample 1	March 5, 2003
Sample 2	March 5, 2003
Sample 3	March 5, 2003
Sample 4	March 5, 2003
Sample 5	March 5, 2003
Sample 6	March 5, 2003

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.04		0.1	0.09	1.9
Sample 2	0.06		17.3	1.28	68.3
Sample 3	0.02		35.6	2.16	139.5
Sample 4	0.04		0.0	0.11	1.9
Sample 5	0.91		13.6	1.10	75.8
Sample 6	0.29		39.0	2.80	137.2

Brief descriptions of analysis:
Nutrients were analyzed using a Bran+Luebbe TRAACS 800 autoanalyzer following the protocol for the JGOFS core measurements with low-nutrient seawater (LNSW) base.

Laboratory 9

LABORATORY: R/V *Ryofu-Maru*

DATE OF RECEIPT OF SAMPLES:

DATA OF ANALYSIS:

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.01 ± 0.00		0.04 ± 0.04	0.08 ± 0.00	1.80 ± 0.06
Sample 2	0.16 ± 0.00		16.39 ± 0.04	0.99 ± 0.00	62.99 ± 0.06
Sample 3	0.00 ± 0.00		35.17 ± 0.04	2.03 ± 0.00	129.10 ± 0.06
Sample 4	0.01 ± 0.00		0.03 ± 0.04	0.10 ± 0.00	1.89 ± 0.06
Sample 5	0.90 ± 0.00		13.84 ± 0.04	1.02 ± 0.00	69.64 ± 0.06
Sample 6	0.13 ± 0.00		38.57 ± 0.04	2.56 ± 0.00	127.06 ± 0.06

Laboratory 10

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY: Oceanographical Division, Maizuru Marine Observatory

DATE OF RECEIPT OF SAMPLES: 15 January 2003

DATA OF ANALYSIS:

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.00 ± 0.01	0.00 ± 0.14	0.00 ± 0.14	0.10 ± 0.05	—
Sample 2	0.06 ± 0.01	18.28 ± 0.14	18.34 ± 0.14	1.25 ± 0.05	—
Sample 3	0.00 ± 0.01	35.15 ± 0.14	35.15 ± 0.14	2.00 ± 0.05	—
Sample 4	0.00 ± 0.01	0.00 ± 0.14	0.00 ± 0.14	0.12 ± 0.05	—
Sample 5	0.88 ± 0.01	13.39 ± 0.14	14.27 ± 0.14	1.09 ± 0.05	—
Sample 6	0.42 ± 0.01	37.15 ± 0.14	37.57 ± 0.14	2.71 ± 0.05	—

Brief descriptions of analysis:
We measured these samples with an AA-II system.
measurement dates: 17–18 March 2003
measurement place: R/V *Seifu Maru* (at Maizuru)

Laboratory 11

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY: IFREMER Centre de BREST
Département DEL/EC/PP
BP 70
29280 Plouzane, France

DATE OF RECEIPT OF SAMPLES: 15/01/2003

DATA OF ANALYSIS:
Sample 1: Nitrate, Nitrite, Phosphate, 12/03/03; Silicic acid, 13/03/03
Sample 2: Nitrate, Nitrite, Phosphate, 12/03/03; Silicic acid, 13/03/03
Sample 3: Nitrate, Nitrite, Phosphate, 12/03/03; Silicic acid, 13/03/03
Sample 4: Nitrate, Nitrite, Phosphate, 12/03/03; Silicic acid, 13/03/03
Sample 5: Nitrate, Nitrite, Phosphate, 12/03/03; Silicic acid, 13/03/03
Sample 6: Nitrate, Nitrite, Phosphate, 12/03/03; Silicic acid, 13/03/03

Results in micromoles per kilogram

	NO_2	NO_3	$NO_3 + NO_2$	PO_4	Si
Sample 1	0.02 ± 0.01	0.08 ± 0.1	0.10 ± 0.1	0.13 ± 0.02	2.1 ± 0.1
Sample 2	0.22 ± 0.01	16.8 ± 0.1	17.0 ± 0.1	1.28 ± 0.02	70.1 ± 0.1
Sample 3	0.01 ± 0.01	34.8 ± 0.1	34.9 ± 0.1	2.19 ± 0.02	136 ± 1
Sample 4	0.02 ± 0.01	0 ± 0.1	0 ± 0.1	0.08 ± 0.02	2.08 ± 0.1
Sample 5	0.96 ± 0.01	11.7 ± 0.1	12.7 ± 0.1	1.12 ± 0.02	77.5 ± 0.1
Sample 6	0.39 ± 0.01	36.7 ± 0.1	37.0 ± 0.1	2.77 ± 0.02	134 ± 1

Brief descriptions of analysis:
Nitrate and phosphate were automatically analyzed with an Technicon AACE Autoanalyser, and nitrite and silicic acid with an Technicon AAII Autoanalyser.
The technical reference manual for analysis is “Manuel d’analyse des sels nutritifs dans l’eau de mer” (Utilisation de l’Autoanalyser II Technicon) – P. Treguer, P. Le Corre, 1975.

Your comments: none

Laboratory 13

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY:

The R/V *Mirai*

DATE OF RECEIPT OF SAMPLES:

Jan. 19, 2003

DATE OF ANALYSIS:

Sample 1	**Mar. 13, 2003**
Sample 2	**Mar. 13, 2003**
Sample 3	**Mar. 13, 2003**
Sample 4	**Mar. 13, 2003**
Sample 5	**Mar. 13, 2003**
Sample 6	**Mar. 13, 2003**

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	**0.02**	**0.07**	**0.09**	**0.09**	**1.38**
Sample 2	**0.19**	**17.32**	**17.51**	**1.19**	**65.62**
Sample 3	**0.01**	**35.23**	**35.24**	**2.10**	**133.97**
Sample 4	**0.01**	**0.05**	**0.05**	**0.08**	**1.48**
Sample 5	**0.90**	**12.86**	**13.76**	**1.05**	**72.30**
Sample 6	**0.14**	**38.83**	**38.97**	**2.74**	**131.50**

Brief descriptions of analysis:

System used: BRAN+LUEBBE TRAACS 800

Your comments:

We feel uncertain as to the values of nitrite + nitrate and silicic acid for sample 4.

To evaluate the overall performance of our measuring system, we measured concentrations of nutrients in the intermediate layer of the western North Pacific, and calculated the repeatability ($n = 5$). The results are as follows:

0.01 ± 0.003 (average ± 1 SD) for nitrite; 36.52 ± 0.047 for nitrate; 36.53 ± 0.044 for nitrite + nitrate; 2.52 ± 0.005 for phosphate; and 146.09 ± 0.267 for silicic acid. This evaluation is close to that of the measuring system during the cruise of the *Mirai* (MR03-K01).

Laboratory 14

2003 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix

RESULTS REPORT FORM

LABORATORY:
KEIFUMARU

DATE OF RECEIPT OF SAMPLES:
1 7 APRIL 2003

DATA OF ANALYSIS:

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.00	0.02	0.02	0.07	
Sample 2	0.22	16.89	17.11	1.25	
Sample 3	0.00	35.66	35.66	2.27	
Sample 4	0.00	0.00	0.00	0.05	
Sample 5	0.89	13.29	14.19	1.15	
Sample 6	0.23	38.85	39.08	2.91	

Brief descriptions of analysis: The analytical method is the oceanographic observation guideline (JMA)
Samples were analyzed on an AAII instrument

Comments: 3 is analyzed, and it third.
Shown value the salinity used for the calculation.
Nitrite + nitrate of reduction is 98%
Water temperature 26 ºC (room temperature)

Laboratory 15

RESULTS REPORT FORM

LABORATORY:
Nagasaki Marine Observatory

DATE OF RECEIPT OF SAMPLES:

DATA OF ANALYSIS:

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.00 ± 0.00	0.02 ± 0.18	0.02 ± 0.18	0.06 ± 0.01	
	------------	-------------	--------------	------------	-----------
Sample 2	0.16 ± 0.00	17.71 ± 0.18	17.87 ± 0.18	1.24 ± 0.01	
	------------	-------------	--------------	------------	-----------
Sample 3	0.01 ± 0.00	35.78 ± 0.18	35.79 ± 0.18	2.21 ± 0.01	
	------------	-------------	--------------	------------	-----------
Sample 4	0.02 ± 0.00	0.06 ± 0.18	0.08 ± 0.18	0.09 ± 0.01	
	------------	-------------	--------------	------------	-----------
Sample 5	0.94 ± 0.00	13.24 ± 0.18	14.18 ± 0.18	1.12 ± 0.01	
	------------	-------------	--------------	------------	-----------
Sample 6	0.15 ± 0.00	39.99 ± 0.18	40.14 ± 0.18	2.88 ± 0.01	
	------------	-------------	--------------	------------	-----------

Brief descriptions of analysis:
The sample subdivided to the sample cup of three, and analyzed six samples at the same time.
The analytical error is a standard deviation of the standard.

Laboratory 16

RESULTS REPORT FORM

LABORATORY: KANSO

DATE OF RECEIPT OF SAMPLES:
2003/1/17

DATA OF ANALYSIS:
Sample 1 2003/4/16
Sample 2 2003/4/16
Sample 3 2003/4/16
Sample 4 2003/4/16
Sample 5 2003/4/16
Sample 6 2003/4/16

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.03 ± 0.00	0.12 ± 0.03		0.18 ± 0.01	1.71 ± 0.03
	------------	-------------	--------------	------------	-----------
Sample 2	0.13 ± 0.00	17.47 ± 0.04		1.17 ± 0.01	64.71 ± 0.34
	------------	-------------	--------------	------------	-----------
Sample 3	0.02 ± 0.00	35.80 ± 0.10		2.19 ± 0.02	136.30 ± 0.62
	------------	-------------	--------------	------------	-----------
Sample 4	0.04 ± 0.00	0.08 ± 0.00		0.20 ± 0.01	1.85 ± 0.07
	------------	-------------	--------------	------------	-----------
Sample 5	0.94 ± 0.00	13.07 ± 0.06		1.18 ± 0.01	73.03 ± 0.50
	------------	-------------	--------------	------------	-----------
Sample 6	0.18 ± 0.00	36.85 ± 0.14		2.82 ± 0.02	136.27 ± 0.19
	------------	-------------	--------------	------------	-----------

Brief descriptions of analysis:
Nutrient analysis was performed on two Bran+Luebbe TRAACS 2000 systems with 4-channel analyzing systems for nitrate, nitrite, silicic acid, and phosphate.

Nitrite: Nitrite was determined by diazotizing with sulfanilamide and coupling with *N*-1-naphthyl-ethylenediamine to form a colored azo dye whose absorbance was measured at 550 nm using a 5-cm-long cell.

Nitrate: Nitrate in seawater was reduced to nitrite in a reduction tube (Cd–Cu tube), and the nitrite determined by the method described above, but the flow cell used in nitrate analysis was 3-cm-long cell.

Phosphate: The method of Murphy and Riley (1962) was used with separate additions of ascorbic acid and mixed molybdate–sulfuric acid–tartrate. The absorbance of the phosphomolybdate produced was measured at 880 nm using a 5-cm-long cell.

Silicic acid: The standard AAII molybdate–ascorbic acid method was used. The temperature of the sample was maintained at 45–50 ºC using a water bath to reduce the reproducibility problems encountered when the samples were analyzed at different temperatures. The absorbance of the silicomolybdate produced was measured at 660 nm using a 3-cm-long cell.

Laboratory 17

RESULTS REPORT FORM

LABORATORY:
Hokkaido National Fisheries Research Institute, Fisheries Research Agency
(116 Katsurakoi, Kushiro, 085-0802 Hokkaido, Japan)

DATE OF RECEIPT OF SAMPLES:
March 2003

DATA OF ANALYSIS:

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	0.045	0.05		0.078	2.29
Sample 2	0.118	18.10		1.320	66.63
Sample 3	0.048	37.10		2.143	135.19
Sample 4	0.050	0.23		0.074	2.61
Sample 5	0.968	13.71		1.118	73.74
Sample 6	0.241	37.74		2.690	133.46

Brief descriptions of analysis:
Samples were measured on April 22 and 23, 2003.
Each reported value is the mean of 4 measurements.

Laboratory 18

RESULTS REPORT FORM

LABORATORY:
Seikai National Fisheries Research Institute

DATE OF RECEIPT OF SAMPLES:
Maybe mid January 2003

DATA OF ANALYSIS:

Results in micromoles per kilogram (mean ± standard deviation)

	Nitrite	Nitrate	Nitrite + nitrate	Phosphate	Silicic acid
Sample 1	------------	-------------	0.07 ± 0.03	0.10 ± 0.02	0.12 ± 0.23
Sample 2	------------	-------------	17.78 ± 0.09	1.19 ± 0.01	66.08 ± 0.19
Sample 3	------------	-------------	35.41 ± 0.08	2.06 ± 0.01	136.83 ± 0.58
Sample 4	------------	------------	0.05 ± 0.03	0.13 ± 0.02	0.32 ± 0.23
Sample 5	------------	-------------	14.09 ± 0.04	1.06 ± 0.02	73.21 ± 0.27
Sample 6	------------	-------------	38.47 ± 0.23	2.71 ± 0.01	134.95 ± 0.54

Appendix III

Documents

Appendix III – Documents
III – 1 Call for participating

Dear Colleague,

This letter is to invite you to “Intercomparison Exercise for Reference Material of for Nutrients in Seawater in a seawater matrix 2003”.

Progress in Reference Material for Nutrients in Seawater (RMNS) has done by our group during these five years. The seawater in a stainless steel container of 40 liters was autoclaved at 120 deg. C, 2 hours, 2 times. The autoclaved seawater of 90 ml was filled in polypropylene bottles. The homogeneity of the RMNS was confirmed as same magnitude as a repeatability of the measurements of the same sample. The long-term storage experiment of our RMNS for up to 4 years showed that homogeneity and concentrations of nutrient are maintained for about 4 years. Our results, then, had demonstrated that the RMNS for nitrate, nitrite, phosphate and silicic acid can be obtained using autoclaving and can be stored for about up to 4 years.

The objectives of this effort are to establish traceability on nutrient analyses in seawater and to become the onboard nutrients analyses more easy where more accurate nutrients data could become available. We also focused to provide the certified reference material in this field. Although the Group of Expert on standards and Reference Material had clearly pointed out (UNESCO, 1991,1992) the necessity of giving high priority to developing production of RMNS, the Certified Reference Materials which are in a seawater matrix are not available in this field at this moment. The only way now is to conduct inter-laboratory comparison experiments by laboratories, which would provide consensus values and their uncertainty of nutrients concentrations for nitrate, nitrite, phosphate and silicic acid.

The reply sheet in a document 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 November 2002, you will not receive any RMNS samples.

2. I will acknowledge receipt of your reply and list of the participants on 3 Dec. 2002. If you do not receive an acknowledgement by 7 Dec. 2002, please contact us in case your reply has gone elsewhere.

3. A reply sheet will confirm that your wish to participate this comparison exercise and to analyzing the samples and submitting results before the reporting deadline, tentatively end of April 2003, 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 silicic acid.

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 an anonymous ftp site of our Institute. You will find three files, two of them are posters presented at Ocean Sciences Meeting at Hawaii in Feb. 2002 and one of them are draft of manuscript entitled "Reference material for nutrients in seawater in a seawater matrix". The site is mri-2.mri-jma.go.jp, you can login as anonymous user using your e-mail address. The files are at /pub/geochem/outging/OSM.

Best regards,

Michio AOYAMA

Intercomparison Exercise for Reference Material of for Nutrients in Seawater in a seawater matrix 2003

IMPORTANT DATES

DEADLINE OF REPLY: 30 NOVEMBER 2002.

LIST OF PARTICIPANT: 3 DECEMBER 2002.

SAMPLES SHIPPED BY : 10 JANUARY 2003

REPORTING DEADLINE: 30 APRIL 2003

EXPECTED DRAFT OF INTERCOMPARIOSN SUMARY: 30 JUNE 2003
"Intercomparison Exercise for Reference Material of for Nutrients in Seawater in a seawater matrix 2003".

III – 2 Instructions for RMNS bottles

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

2. Preparations of samples
1) No preservatives have been added.
2) The details of preparation are given in the documents at our anonymous ftp site. You will find three files, two of them are posters presented at Ocean Sciences Meeting at Hawaii in Feb. 2002 and one of them are draft of manuscript entitled "Reference material for nutrients in seawater in a seawater matrix". The site is mri-2.mri-jma.go.jp, you can login as anonymous user using your e-mail address. The files are at /pub/geochem/outging/OSM.

3. Analysis
1) RMNSs are ready for analysis, then please use them without filtration just after you open the bottles. Again, no preservatives have been added, when opened their sterility will be lost.
2) Salinities are in the range 34.5-34.8.

Sample 1	34.75+-0.10
Sample 2	34.65+-0.10
Sample 3	(assumed to be 34.65)
Sample 4	34.80+-0.10
Sample 5	34.60+-0.10
Sample 6	34.50+-0.10

I will determine the salinity of sample3 and deliver them to the participants later. Then please use 34.65 as the tentative salinity of sample3 to get the density of sample3.
3) Concentrations can be assumed to be in the following ranges in micromoles per kilogram. Atlantic people may be surprised by high concentrations of sample 3 and 6, however, these RMNS are Pacific origin.

	Nitrite	Nitrate	Nitrite + Nitrate	Phosphate	Silicic acid
Sample 1	<0.5 ------------	<5 ------------		<0.5 ------------	<5 ------------
Sample 2	<0.5 ------------	<20 ------------		<1.5 ------------	<80 ------------
Sample 3	<0.5 ------------	<45 ------------		<3.0 ------------	<150 ------------
Sample 4	<0.5 ------------	<5 ------------		<0.5 ------------	<5 ------------
Sample 5	<1.2 ------------	<20 ------------		<1.5 ------------	<80 ------------
Sample 6	<1.0 ------------	<45 ------------		<3.0 ------------	<150 ------------

4. Reporting of results

1) Report concentrations in micromoles per kilogram using the reporting format attached.
2) Please report one value for each parameter for each sample.
3) Participants are welcome to add your estimation on analytical error for each parameter for each sample (ex. 1.23±0.04; 23.45±0.67).
4) REPORTING DEADLINE: 30 APRIL 2003

Intercomparison Exercise for Reference Material of for Nutrients in Seawater in a seawater matrix 2003

Appendix III- 3 Results report form

LABORATORY:

DATE OF RECEIPT OF SAMPLES:

DATA OF ANALYSIS: SAMPLE 1
SAMPLE 2
SAMPLE 3
SAMPLE 4
SAMPLE 5
SAMPLE 6

Results in micromoles per kilogram

	Nitrite	Nitrate	Nitrite + Nitrate	Phosphate	Silicic acid
SAMPLE 1	------------	------------		------------	------------
SAMPLE 2	------------	------------		------------	------------
SAMPLE 3	------------	------------		------------	------------
SAMPLE 4	------------	------------		------------	------------
SAMPLE 5	------------	------------		------------	------------
SAMPLE 6	------------	------------		------------	------------

Options;
Brief descriptions of analysis;

Your comments;

THESE RESULTS SHOULD BE SENT TO: Michio AOYAMA
maoyama@mri-jma.go.jp
or mail to
Michio AOYAMA
Geochemical Res. Dep.
Meteorological Res. Inst.
1-1 Nagamine,305-0052
JAPAN

Appendix IV

History of nutrients intercomprisons

Appendix IV History of nutrient intercomparisons

This history of nutrient intercomparisons is based on several reports of previous intercomparison exercises. The histories of the first to fourth ICES exercises are derived from Aminot and Kirkwood's (1995) detailed report of the fifth ICES intercomparison, which includes histories of the first to fourth ICES exercises. Histories of the fifth ICES exercise and the first and second NOAA/NRC intercomparisons are also summarized in this appendix.

1. First ICES Exercise

The first intercalibration to include nutrients was an entirely Baltic affair in June 1965, when 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 to the experiment, 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 still predominantly a Baltic initiative and consisted of two parts: Part I, Leningrad, during the 5th Conference of Baltic Oceanographers; and Part II, Copenhagen, at the 54th ICES Statutory Meeting.

Part I, Leningrad (May 1966)

The participating research vessels were

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, Copenhagen (September 1966)

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 various participants analyzed samples simultaneously in Copenhagen. The determinands of primary interest included not only oxygen, salinity, chlorinity, and phosphate, as in Part I (Leningrad) and the previous year's exercise (Copenhagen, 1965), 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 confessed that these results were "too terrible to be included"! To be fair to those involved, 1966 was an early time in the development of heterogeneous cadmium-based nitrate/nitrite reduction techniques and some of the associated problems were presumably not fully appreciated at the time.

Evidently nitrate analysis had some way to go to achieve the reliability and ease of operation of the Murphy and Riley (1962) phosphate technique, but it is worth noting that intercomparison work on phosphate so far had consisted of simultaneous analysis of freshly obtained subsamples by a small number of highly competent workers, in close contact with each other, exchanging calibration solutions, ideas, technical details, etc. Subsequent to the Copenhagen trial, 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 Methods2”, shows that it set out to be an ambitious project.

Samples were distributed in 1969–1970 and 45 laboratories from 20 countries submitted results, but 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 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 being supplied (knowingly) 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 them together. Hindsight suggests that this 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 are aware that it is producing poor quality data.

4. Fourth ICES Exercise

Various "workshop" and multiship events following the ICES/SCOR exercise included nutrient studies, but it was many years later (1988) before the ICES Marine Chemistry Working Group produced volunteers (Don Kirkwood, Alain Aminot, and Matti Perttilä) to organize the next large-scale intercalibration exercise, designated "NUTS I/C 4". This exercise did not set out to be worldwide, beginning only with laboratories in ICES Member Countries, but other laboratories who were interested in participating were not turned away.

The fourth exercise differed from the third exercise 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 intercomparison rather than an intercalibration.)
2) Participants were unaware that "blank" samples were included.
3) Anonymity was abolished. Participants were made aware from the outset that the final report would list identities of laboratories, results, and a means for any reader to contact them.

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

Due to the generally perceived need for more and better quality control in analytical measurement, a fifth ICES intercomparison exercise 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 intercomparison and 56 of which were participating in QUASIMEME (Quality Assurance of Information for Marine

Environmental Monitoring in Europe). The distribution of 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), Turkey(1),

The method of sample preparation, autoclaving, for the fifth intercomparison 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 salt. Although the concentrations in the distributed samples covered a greater concentration range than that in the fourth intercomparison, the concentration levels were 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 Intercomparison

The test material distributed in this intercomparison was MOOS-1, a proposed certified 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 requested to perform duplicate analyses on each of the bottles. The prepared samples were sent to 36 participating laboratories. Thirty sets of results were returned.

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

7. 2002 NOAA/NRC Intercomparison

An intercomparison exercise was undertaken to assess the current capabilities of a group of laboratories to quantitate orthophosphate, silicate, nitrite, and nitrite + nitrate in a seawater sample. This was the second such exercise sponsored by the NOAA Center for Coastal Monitoring and Assessment (CCMA) and coordinated by the Institute for National Measurement Standards of the National Research Council of Canada. Two seawater samples — one from Pensacola Sound, FL, 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 intercomparison exercise was overcome, although the orthophosphate data indicate a larger interlaboratory spread of results than expected.

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

8. 2003 MRI Intercomparison

Autoclaved natural seawater was prepared for intercomparison samples. Sample homogeneity was confirmed by repeatability of measurement. Sets of 6 samples covering a concentration range greater than that in previous intercomparisons were distributed. The concentrations were 0–38 µmol kg–1 for nitrate, 0–0.9 µmol kg–1 for nitrite, 0–2.7 µmol kg–1 for phosphate, and 0–136 µmol kg–1 for silicic acid. A total of 18 sets of samples were distributed to 18 laboratories in 5 countries. Results were returned by 17 laboratories in 5 countries. Although consensus concentrations were obtained for the 6 samples, the standard deviations were 4.5 times and more than 10 times greater than those of the homogeneities for phosphate and silicic acid, respectively. For nitrate, the standard deviations were only about double the homogeneities. These results indicate that variability in in-house standards of the participating laboratories — rather than analytical precision — is the primary source of interlaboratory discrepancy. Therefore use of a certified RMNS is essential for establishing nutrient data sets that can be compared across laboratories, especially for silicic acid and phosphate.