1. Introduction

The objective of this inter-laboratory comparison (I/C) study was to develop a reference material for analysis of nutrients in seawater that would ensure comparability of analytical data collected by different laboratories, and that would facilitate shipboard analysis of nutrients in seawater. Highly accurate nutrient data from different laboratories could thus become more widely available. We have focused on developing a certified reference material for nutrients in seawater (hereafter, RMNS) within a seawater matrix. The IOC - International Atomic Energy Agency (IAEA) - United Nations Environment Programme (UNEP) Group of Experts on Standards and Reference Materials (UNESCO, 1991, 1992) has clearly stated the need to place a high priority on developing a reference material for nutrients in seawater.

However, as stated in the report entitled "Climate Change 2007 – The Physical Science Basis" (Bindoff, et al., 2007), adequate comparability and traceability have not yet been achieved. This report comments on nutrient comparability as follows:

> "Using the same data set extended to the world, large regional changes in nutrient ratios were observed but no consistent basin-scale patterns. Uncertainties in deep ocean nutrient observations may be responsible for the lack of coherence in the nutrient changes. Sources of inaccuracy include the limited number of observations and the lack of compatibility between measurements from different laboratories at different times".

Previously, the way to ensure comparability among nutrient analyses performed by different laboratories was to conduct I/C studies that provided consensus values plus uncertainties for nutrient concentrations. The International Council for the Exploration of the Sea (ICES) Nutrient Inter-comparison has been carried out five times since 1965 (UNESCO, 1965, 1967; ICES, 1967, 1977; Kirkwood *et al.*, 1991; Aminot and Kirkwood, 1995), and other efforts to ensure comparability among nutrient analyses in sea water have been carried out for over 30 years. In 2000 and 2002, the National Oceanic and Atmospheric Administration (NOAA)/National Research Council Canada (NRC) inter-comparisons between laboratories in the United States and Canada were carried out to certify a seawater reference material for nutrients known as MOOS-1, which was provided by the NRC (Willie and Clancy, 2000; Clancy and Willie, 2003).

In 2003 and 2006, the Meteorological Research Institute of Japan (MRI) conducted I/C studies with two main differences from previous studies. First, the nutrient concentrations in 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 four determinants (nitrate, nitrite, phosphate, and silicate) could be simultaneously analyzed.

In the 2003 I/C study, the consensus standard deviations were 4.5 times the homogeneities for phosphate and more than 10 times those of silicate. For nitrate, the standard deviations were only about double the homogeneities. These results indicated that the variability between “in-house” standards in the participating laboratories, rather than analytical precision, was the primary source of inter-laboratory differences.

In the 2006 I/C study, analytical precisions reported from the participating laboratories for all determinants were more precise as less than 50% of the consensus standard deviations of reported concentrations. Consensus standard deviations of Sample2, which had the highest concentrations for all determinants among the samples used in the 2006 I/C study, were five to ten times the homogeneities of Sample2 for all determinants. In some laboratories, the non-linearity of the calibration curve was not addressed effectively.

The results obtained in both the 2003 and 2006 I/C studies indicated that the variability between the in-house standards of the participating laboratories and the way that the participating laboratories handled the non-linearity of their instruments were the primary sources of inter-laboratory discrepancies. Therefore it became evident that both the use of a certified reference material and the use of common methodologies for nutrient measurements are essential for improving and establishing global comparability and traceability of nutrient data in the world's oceans.

In 2008, an I/C study was conducted using a strategy similar to the strategies used for the 2003 and 2006 studies. In the 2008 RMNS I/C study, two of the samples were from the same batch as those used in the 2006 RMNS I/C study. Therefore it is possible to compare nutrient data from the same laboratories in 2006 and 2008.

This report describes the 2008 I/C study in detail and summarizes the results reported by the participants. This report also discusses the comparability between results of the 2006 and 2008 I/C studies.

2. Samples

2.1 Sample preparation and timetable for the inter-laboratory comparison study

Natural seawater was collected in the North Pacific Ocean and depth of surface, and nutrient concentration maximum depth around 1500m. Seawater was placed into a 230-L stainless steel container and autoclaved twice at 120 ºC for 2 h. Aliquots of 90 mL of the autoclaved seawater were then transferred into polypropylene bottles. This procedure for preparing 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). The sample homogeneity was confirmed by repeatability of analytical measurements. Long-term storage of our RMNS samples for up to 4 years at room temperature has shown that the homogeneities and concentrations of nutrients are maintained for about at least this length of time (Aoyama *et al.*, 2007).

The samples sent to the participants in this study were prepared from 2005 to 2007. The nutrient concentrations in the samples were confirmed as stable for at least several months before the samples were sent out to the participants. Fifty-four participants had analyzed the samples and returned the results by January 2009.

Salinities of samples ranged from 34.27 ± 0.01 to 34.63 ± 0.01, and participants were provided the salinities of the samples to calculate density of sample seawater when they analyze them. (See Appendix IV for salinities of samples.)

The nutrient concentrations were not provided to participants during the I/C study; however, maximum concentrations were provided, and indicated as less than 1 μmol kg^{-1} for nitrite, less than 45 μmol kg^{-1} for nitrate, less than 3.5 μmol kg^{-1} for phosphate, and less than 170 μmol kg^{-1} for silicate (see Appendix IV).

2.2 Selection of determinants

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

2.3 Sample homogeneity

The homogeneities of the samples were measured separately. The homogeneities for 30 bottles of Sample3, which had the highest nutrient concentrations among the samples used in this I/C study, are listed in Table 1. The homogeneities of Sample2 from the 2006 I/C study and Sample3 from the 2003 I/C study, each with the highest nutrient concentrations for their respective studies, are also shown in Table 1. As shown in Table 1, the homogeneities of Sample3 in 2008 for three determinants were much improved over those of Sample2 in 2006 and Sample3 in 2003.

In addition, the analytical precision was estimated for 30 samples of natural seawater collected at deep layers in the North Pacific Ocean with nutrient concentrations similar to those of Sample3 in the 2008 I/C study.

Table 1. Homogeneity of samples with the highest nutrient concentrations in I/C studies in 2003, 2006, and 2008, and the analytical precision of 30 seawater replicate analyses in 2008.

	Nitrate+Nitrite	Phosphate	Silicate	Nitrite
Homogeneity of Sample3 (%)	0.11	0.21	0.10	37*
Analytical precision in 2008 (CV, %)	0.05	0.07	0.06	
Homogeneity of Sample2 used in the 2006 I/C study (%)	0.22	0.32	0.19	
Homogeneity of Sample3 used in the 2003 I/C study (%)	0.44	0.80	0.15	

The nutrient concentrations in natural seawater samples used to measure analytical precision were nitrate+nitrite, 43 μmol kg^{-1}; phosphate, 3.1 μmol kg^{-1}; silicate, 148 μmol kg^{-1}.

*The homogeneity of nitrite for Sample3 (nitrite, 0.016 μmol kg^{-1}) is based on 87 analyses onboard the R/V *Mirai* MR0704.

3. Participants and response

By September 2008, 58 laboratories in 15 countries had replied to the call for participants. A total of 58 sets of six samples (from Sample 1 to Sample 6) were then distributed. The participating laboratories are listed Table A1 in Appendix I and are cross-referenced by laboratory number to the laboratories participating in the 2003 and 2006 I/C studies in Table A2.

Results were returned from 55 laboratories as of 4 February 2009. Table 2 summarizes the data responses from participants.

Table 2. Summary of responses from participants.

Nutrient	Sample #	Number of results	
		Received	Statistically treated
Nitrate+Nitrite	1	53	53
	2	52	52
	3	52	52
	4	53	48
	5	52	52
	6	52	52
	7	4	4
	8	0	0
Nitrate	1	45	44
	2	44	43
	3	44	43
	4	43	40
	5	44	43
	6	44	43
	7	4	4
	8	0	0
Nitrite	1	50	50
	2	50	47
	3	50	47
	4	50	46
	5	50	47
	6	50	50
	7	5	5
	8	0	0
Phosphate	1	56	56
	2	56	56
	3	56	56
	4	56	52
	5	56	56
	6	56	56
	7	5	5
	8	0	0
Silicate	1	52	52
	2	52	52
	3	52	52
	4	52	52
	5	52	52
	6	52	52
	7	5	5
	8	0	0

to be continued

Table 2. Summary of responses from participants (continued).

Nutrient	Sample #	Number of results	
		Received	Statistically treated
Ammonia	1	12	
	2	14	
	3	14	
	4	14	
	5	12	
	6	12	
	7	2	
	8	8	
Dissolved organic phosphate (DOP)	1	2	
	2	5	
	3	5	
	4	5	
	5	2	
	6	3	
	7	1	
	8	1	

Nutrient	Sample #	Number of results	
		Received	Statistically treated
Dissolved organic nitrogen (DON)	1	1	
	2	5	
	3	5	
	4	5	
	5	1	
	6	1	
	7	1	
	8	1	
Dissolved organic carbon (DOC)	1	1	
	2	1	
	3	1	
	4	1	
	5	1	
	6	1	
	7	0	
	8	0	

4. Statistical treatment

4.1 Raw mean, median, and standard deviation

The mean, median, and standard deviation of each determinant in each sample were calculated using all reported values (Table 3).

The combined mean, median and standard deviation of Sample 2 and Sample 5 are shown in Table 3, because both samples are same lot of RMNS.

4.2 Robust statistics

Robust means and standard deviations were calculated for each nutrient in each sample using Huber's method, as described by the Analytical Methods Committee (AMC) of The Royal Society of Chemistry (UK) (AMC, 2001) as shown in Table 3. In this method, H15 means and H15 standard deviations were calculated using 1.5 as the multiplier in the Winsorisation process.

4.3 Consensus mean, median, and standard deviation

Successive *t*-tests at the 95% confidence level were applied to the results from all participants before estimating the consensus mean, consensus median, and consensus standard deviation, as in the previous inter-comparison studies (Aminot and Kirkwood, 1995; Aoyama, 2006; Aoyama et al., 2008). Tests were applied until a stable mean was reached; stable means were obtained for each set of results after 7–12 tests. The results of successive *t*-tests are shown in Table 4.

4.4 Calculation of *Z*-scores

Z-scores were used to evaluate the performance of laboratories, as in the previous inter-comparison studies (Aminot and Kirkwood, 1995; Aoyama, 2006; Aoyama et al., 2008). *Z*-scores were calculated for each analysis of each sample at each laboratory as:

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

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

The *Z*-scores for all determinants were calculated and are shown in Tables 7-1 to

7-5.

Combined Z-scores were also calculated for $Z_{NOx} + Z_p$ and $Z_{NOx} + Z_p + Z_s$ for each sample at each laboratory and are shown in Tables 7-6 and 7-7, where Z_{NOx}, Z_p, and Z_s are the Z-scores for nitrate+nitrite, phosphate and silicate, respectively. If concentrations of nitrate+nitrite were not reported, nitrate was used instead.

Table 3. Raw and robust statistics for nutrient concentrations calculated using all reported values.

Nutrient	Sample #	*n*	Raw mean µmol kg^{-1}	Raw median µmol kg^{-1}	Raw SD µmol kg^{-1}	Robust mean µmol kg^{-1}	Robust SD µmol kg^{-1}
Nitrate+Nitrite	1	53	21.51	21.90	1.65	21.83	0.59
	2	52	29.00	29.87	2.64	29.62	0.94
	3	52	41.09	41.36	3.83	41.22	0.89
	4	48	0.14	0.09	0.18	0.10	0.09
	5	52	29.18	29.84	2.34	29.70	0.76
	6	52	6.22	6.30	0.54	6.29	0.23
	7	4	35.93	36.57	1.65	36.04	1.63
	2&5	104	29.09	29.85	2.48	29.66	0.84
Nitrate	1	44	21.43	21.60	0.76	21.51	0.58
	2	43	29.12	29.82	2.02	29.56	0.97
	3	43	41.44	41.34	3.06	41.17	0.93
	4	40	0.12	0.07	0.18	0.07	0.07
	5	43	29.37	29.80	1.38	29.64	0.80
	6	43	5.66	5.68	0.34	5.68	0.23
	7	4	35.85	36.51	1.68	36.02	1.51
	2&5	86	29.25	29.81	1.73	29.61	0.86
Nitrite	1	50	0.35	0.35	0.07	0.35	0.02
	2	47	0.04	0.03	0.04	0.03	0.01
	3	47	0.03	0.02	0.04	0.02	0.01
	4	46	0.04	0.02	0.07	0.02	0.02
	5	47	0.04	0.03	0.04	0.03	0.02
	6	50	0.62	0.63	0.07	0.63	0.03
	7	5	0.07	0.06	0.03	0.07	0.02
	2&5	94	0.04	0.03	0.04	0.03	0.01
Phosphate	1	56	1.59	1.58	0.17	1.58	0.07
	2	56	2.20	2.16	0.20	2.17	0.08
	3	56	2.86	2.80	0.29	2.82	0.11
	4	52	0.11	0.04	0.43	0.04	0.03
	5	56	2.13	2.15	0.31	2.15	0.10
	6	56	0.49	0.49	0.12	0.49	0.05
	7	5	2.73	2.62	0.27	2.65	0.12
	2&5	112	2.16	2.16	0.26	2.16	0.09

Table 3. Mean, median and standard deviation were calculated using reported values (continued).

Nutrient	Sample #	*n*	Raw mean µmol kg^{-1}	Raw median µmol kg^{-1}	Raw SD µmol kg^{-1}	Robust mean µmol kg^{-1}	Robust SD µmol kg^{-1}
Silicate	1	52	59.90	59.62	5.06	59.95	2.56
	2	52	65.43	66.05	7.18	66.23	3.00
	3	52	151.60	152.95	14.73	153.21	5.78
	4	52	1.63	1.67	0.61	1.63	0.38
	5	52	65.77	65.68	5.21	66.00	2.42
	6	52	30.61	30.21	3.51	30.36	1.21
	7	5	262.45	258.38	8.14	262.45	9.22
	2&5	104	65.60	65.75	6.25	66.12	2.70

Robust (H15) means and standard deviations were calculated using Huber’s method with 1.5 as the multiplier in the Winsorisation process (AMC, 2001).

5. Results

Results reported by the participants are summarized in Table A3 in Appendix II.

Raw means, medians, and standard deviations calculated using the reported values are summarized in Table 3 together with the robust statistics.

The median of all reported values ("raw median" in Table 3) for each determinant in six samples is in good agreement with the consensus mean and median (Table 4) for all determinants in six samples.

The robust means for all determinants in six samples (from Sample 1 to Sample 6) are in good agreement with the consensus means and medians for all determinants in six samples.

Scatter plots and histograms of results for each parameter of each sample are shown in Figures A1-6 to A5-6 in Appendix III. The consensus values of median and SD are shown at the top of each figure. In the scatter plots, error bars are included if they were reported with the data. The interval in each histogram is set equal to the corresponding consensus standard deviation.

5.1 Ranked scatter-plots of the results

Figures 1 to 5 are ranked scatter-plots for nitrate+nitrite, nitrate, nitrite, phosphate and silicate, respectively. For nitrate+nitrite, nitrate, phosphate, and silicate, the laboratory results were sorted in order of the concentrations reported for Sample3, which had the highest nitrate, phosphate, and silicate concentrations of the samples sent to the participants. For nitrite, laboratory results were sorted in order of the reported concentrations in Sample6, which had the highest nitrite concentration of all the samples. Error bars are included in Figures 1 to 5 where this information was included with the reported results.

In each of Figures 1 to 5, the ranked concentration plots for a particular nutrient would be proportional and roughly parallel to each other for samples with different nutrient concentrations if each laboratory appropriately compensated for the non-linearity of the calibration curves. However, as evident in Figures 1–5, there are non-proportional results from some laboratories for all of the determinants. According to the information received from several laboratories, a linear calibration was used. This would result in the non-proportional results evident in Figures 1–5 if the calibration curve was in fact non-linear (curved), because the analytical systems used were not optimized for those nutrient values.

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

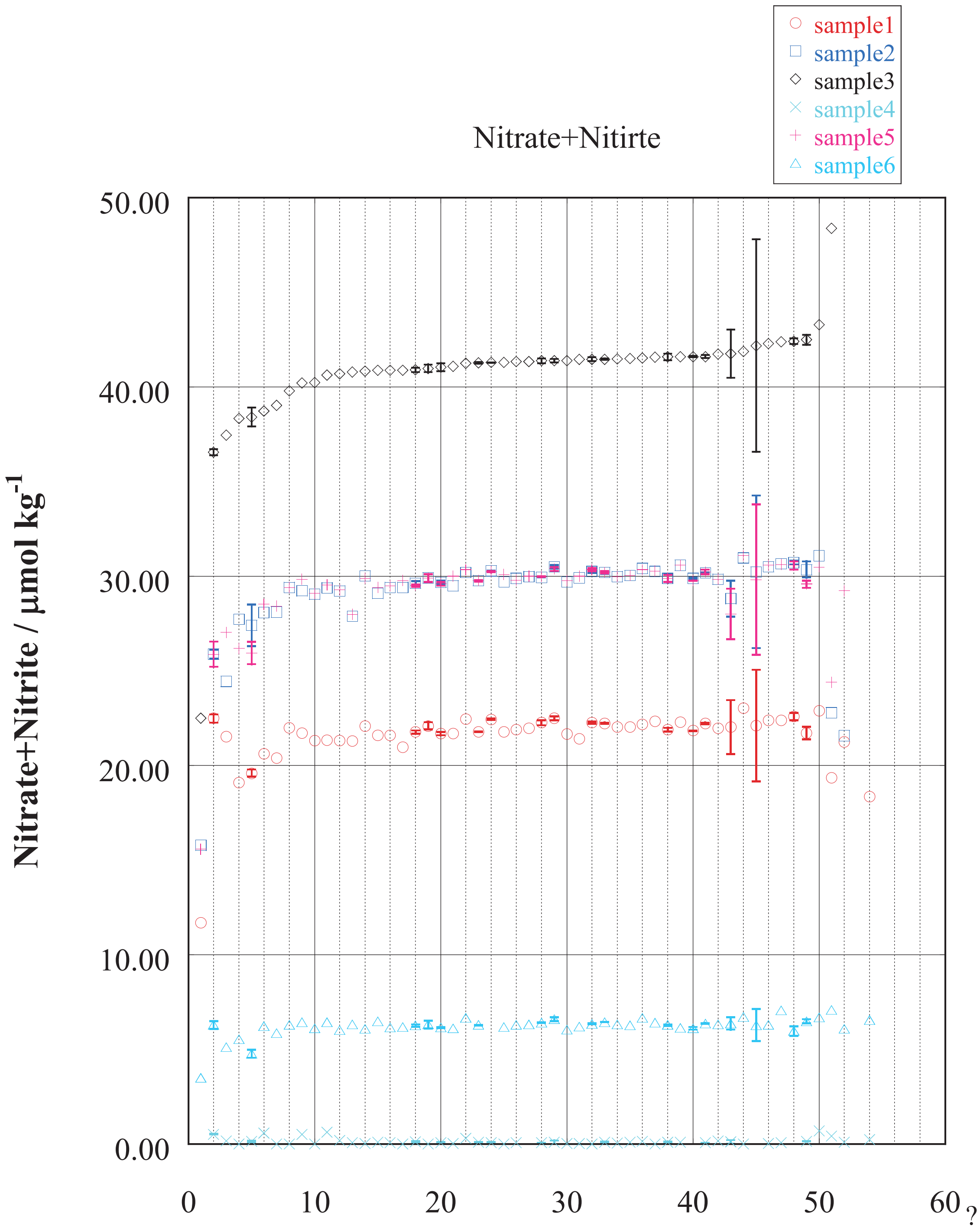

Figure 1. Nitrate+Nitrite results for all samples. Laboratories are ranked in order of concentrations reported for Sample3.

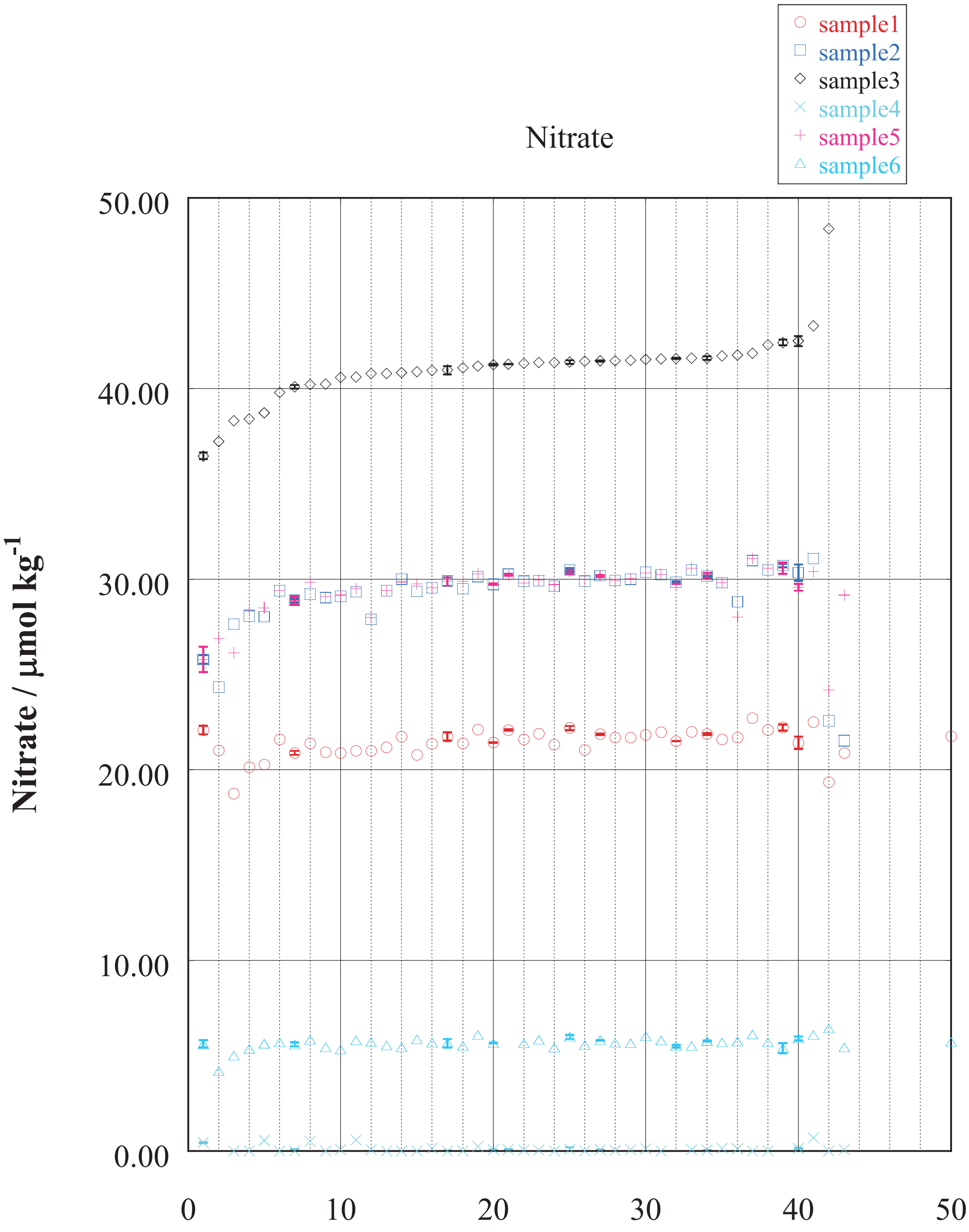

Figure 2. Nitrate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3

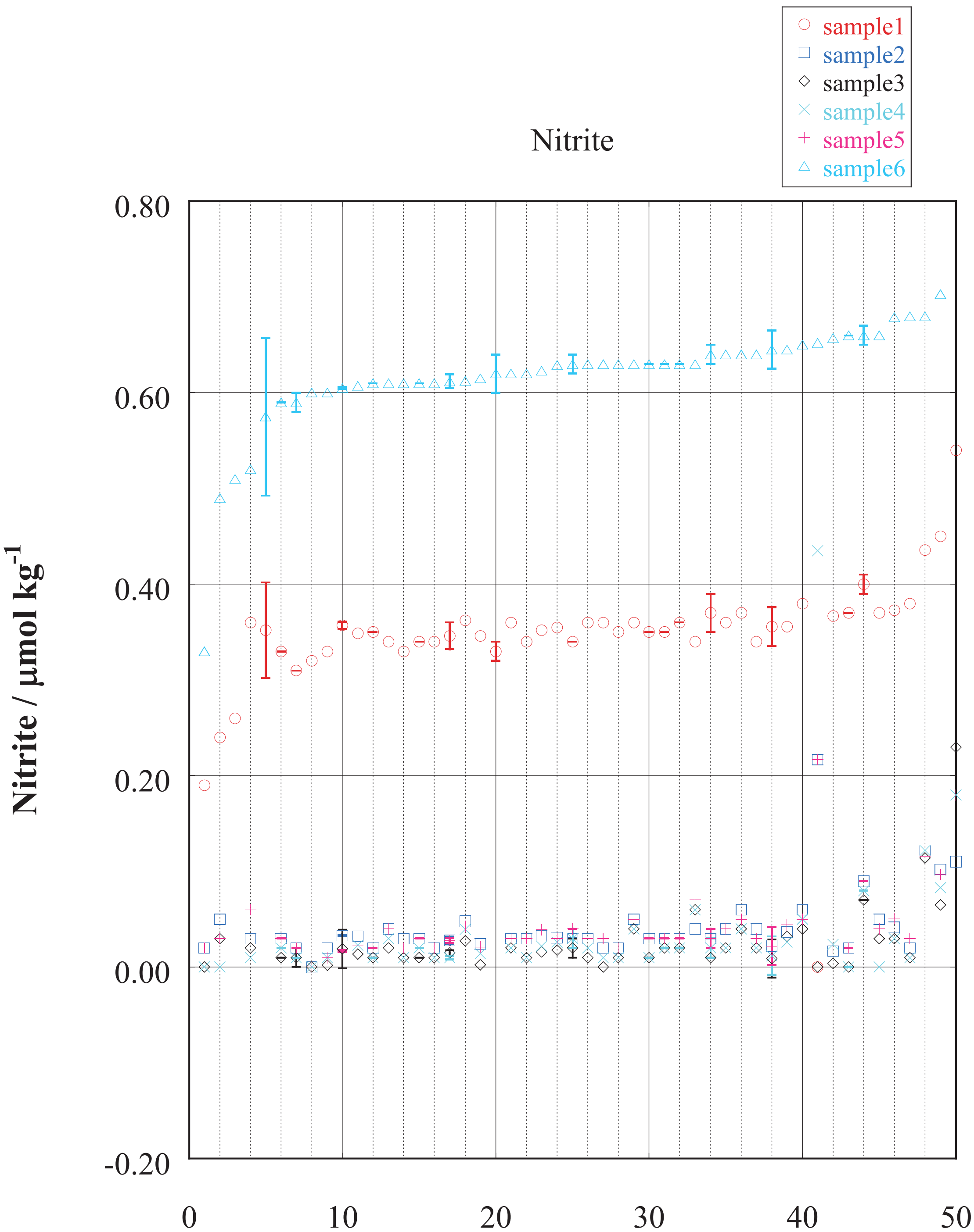

Figure 3. Nitrite results for all samples. Laboratories are ranked in order of concentrations reported for Sample6

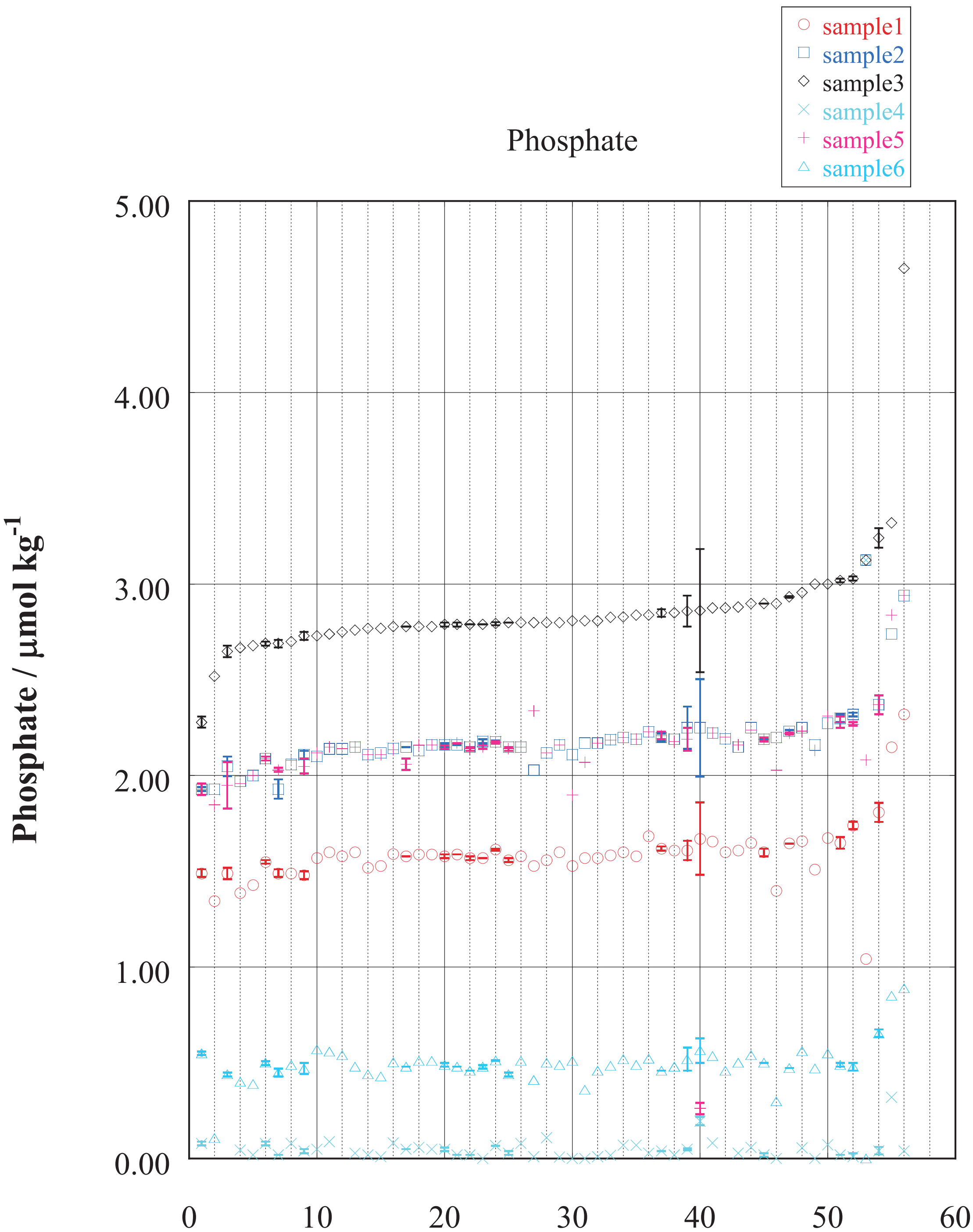

Figure 4. Phosphate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3

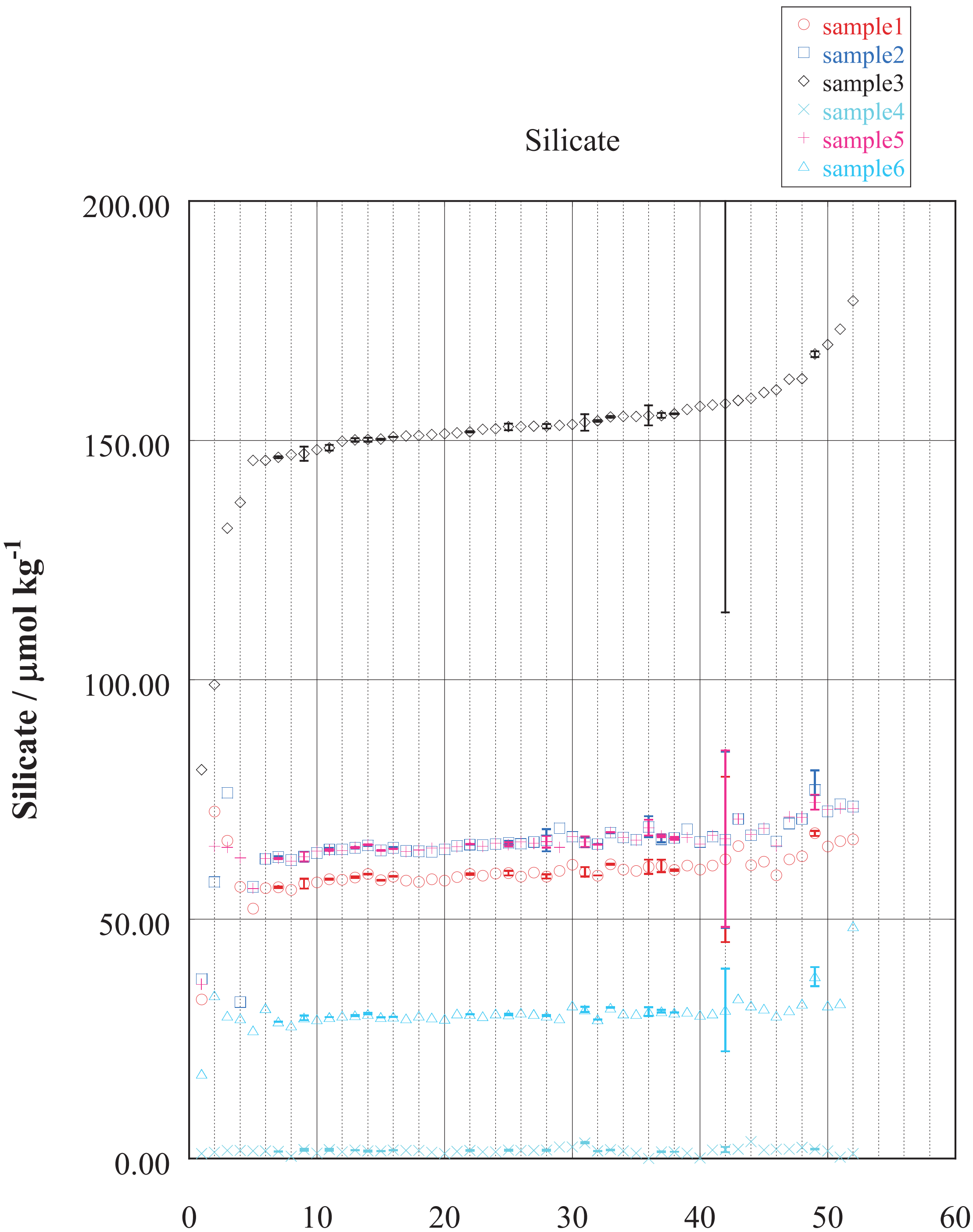

Figure 5. Silicate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3

5.2 Consensus means, medians, and standard deviations

The consensus means, medians, and standard deviations (Table 4) were calculated using the data that passed the successive *t*-test applications described in Section 4.1. The consensus means and medians are in close agreement for all parameters for all samples.

Table 4. Consensus means, medians, and standard deviations for the 7 samples.

Nutrient	Sample	*n**	Consensus mean µmol kg^{-1}	Consensus median µmol kg^{-1}	Consensus SD µmol kg^{-1}
Nitrate+Nitrite	1	43 (53)	21.95	21.98	0.37
	2	39 (52)	29.93	29.92	0.44
	3	33 (52)	41.32	41.39	0.31
	4	40 (48)	0.06	0.07	0.05
	5	40 (52)	29.97	29.95	0.38
	6	37 (52)	6.29	6.30	0.12
	7	4 (4)	35.93	36.57	1.65
	2&5	77 (104)	29.97	29.94	0.39
Nitrate	1	38 (44)	21.55	21.61	0.43
	2	33 (43)	29.83	29.89	0.50
	3	28 (43)	41.28	41.38	0.35
	4	29 (40)	0.03	0.02	0.03
	5	33 (43)	29.91	29.89	0.41
	6	35 (43)	5.64	5.67	0.15
	7	4 (4)	35.85	36.51	1.68
	2&5	64 (86)	29.90	29.90	0.43
Nitrite	1	40 (50)	0.35	0.35	0.01
	2	35 (47)	0.03	0.03	0.01
	3	41 (47)	0.01	0.01	0.01
	4	39 (46)	0.01	0.01	0.01
	5	39 (47)	0.03	0.03	0.01
	6	40 (50)	0.63	0.63	0.02
	7	5 (5)	0.07	0.06	0.03
	2&5	67 (94)	0.03	0.03	0.01

Table 4. Consensus means, medians, and standard deviations for the 7 samples (continued).

Nutrient	Sample	*n**	Consensus mean µmol kg^{-1}	Consensus median µmol kg^{-1}	Consensus SD µmol kg^{-1}
Phosphate	1	47 (56)	1.58	1.59	0.05
	2	41 (56)	2.17	2.16	0.04
	3	38 (56)	2.81	2.80	0.05
	4	51 (52)	0.04	0.03	0.03
	5	37 (56)	2.16	2.16	0.04
	6	42 (56)	0.49	0.49	0.03
	7	5 (5)	2.73	2.62	0.27
	2&5	69 (112)	2.16	2.16	0.03
Silicate	1	41 (52)	59.50	59.45	1.55
	2	31 (52)	65.71	65.74	1.05
	3	40 (52)	152.43	152.68	3.45
	4	37 (52)	1.69	1.72	0.18
	5	35 (52)	65.71	65.60	1.04
	6	35 (52)	30.00	29.94	0.54
	7	5 (5)	262.45	258.38	8.14
	2&5	66 (104)	65.71	65.67	1.04

*Numbers in parentheses are the initial numbers of values before successive *t*-tests reduced the sample size to *n* (see text).

5.3 Comparison between consensus standard deviation and homogeneity of Sample3

For nitrate, the consensus standard deviation in terms of CV was 8 times the homogeneity of nitrate in Sample3 (Table 5). For phosphate and silicate, the consensus CVs were 9 times and more than 20 times the homogeneities in Sample3, respectively.

This indicates that the use of a common reference material for nutrients in seawater would improve the agreement between results from different laboratories and establish global comparability of nutrient data from the world's oceans.

Table 5. Comparison between homogeneity and consensus coefficient of variation of nutrient measurements in Sample3.

	Nitrate	Phosphate	Silicate
Homogeneity (%)	0.11	0.21	0.10
Standard deviation (CV, %)	0.85	1.8	2.2

5.4 Summary of analytical precision of participating laboratories and consensus standard deviation

The analytical precision at participating laboratories and the consensus standard deviation in terms of CV for six samples are summarized in Tables 6-1 to 6-6.

Table 6-1. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample1.

Nutrient	Analytical precision of participating laboratories		Consensus coefficient of variation	
	n	Median (range) %	*n*	CV %
Nitrate+Nitrite	18	0.5 (0.0–13.3)	43	1.7
Phosphate	20	0.9 (0.0–11.3)	47	3.1
Silicate	18	0.3 (0.1–27.6)	41	2.6

Table 6-2. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample2.

Nutrients	Analytical precision of participating laboratories		Consensus CV	
	n	Median (range) %	*n*	CV %
Nitrate+Nitrite	18	0.3 (0–13.3)	39	1.5
Phosphate	20	0.5 (0–11.2)	41	1.9
Silicate	18	0.4 (0–27.6)	31	1.6

Table 6-3. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample3.

Nutrients	Analytical precision of participating laboratories		Consensus CV	
	n	Median (range) %	*n*	CV %
Nitrate+Nitrite	18	0.4 (0–13.3)	33	0.7
Phosphate	20	0.4 (0–11.3)	38	1.8
Silicate	18	0.3 (0–27.6)	40	2.3

Table 6-4. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample4.

Nutrients	Analytical precision of participating laboratories		Consensus CV	
	n	Median (range) %	*n*	CV %
Nitrate+Nitrite	13	20.0 (0.0–100.0)	40	71.4
Phosphate	17	11.2 (0.0–200.0)	51	100
Silicate	18	4.1 (0.0–33.3)	37	10.5

Table 6-5. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample5.

Nutrients	Analytical precision of participating laboratories		Consensus CV	
	n	Median (range) %	*n*	CV %
Nitrate+Nitrite	18	0.4 (0.0–13.3)	40	1.3
Phosphate	20	0.5 (0.0–11.4)	37	1.9
Silicate	18	0.4 (0.0–27.6)	35	1.6

Table 6-6. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample6.

Nutrients	Analytical precision of participating laboratories		Consensus CV	
	n	Median (range) %	*n*	CV %
Nitrate+Nitrite	17	1.0 (0.2–13.3)	37	1.9
Phosphate	20	2.0 (0.0–11.5)	42	6.1
Silicate	18	0.3 (0.0–27.6)	35	1.8

5.5 *Z*-scores

Tables 7-1 to 7-7 present *Z*-scores for participating laboratories computed as described in section 4.4. *Z*-scores indicate how the measurement of a particular determinant in a sample by an individual laboratory compares to the consensus value for that determinant in that sample as determined by all participating laboratories. *Z*-values are proportional to the consensus standard deviation, with a *Z*-value less than 1.0 indicating a measurement within ±1 SD of the consensus median value.

Table 7-1. *Z*-scores for nitrate+nitrite analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	0.2	2.5	1.2	1.2	5.1	0.7
2	0.8	0.8	0.3	1.4	1.1	0.5
3	0.0	0.2	1.2	2.0	0.3	0.2
4	0.5	0.7	1.5	1.2	1.1	0.2
5	0.3	0.1	0.7		0.4	1.5
6	0.2	0.0	0.7	0.6	0.1	0.0
7	0.2	0.0	0.1	0.2	0.4	0.0
9	0.3	0.2	1.7	0.8	0.1	1.6
10						
11	1.4	1.3	0.0	0.6	1.2	2.5
13	1.0	0.8	0.6	1.2	0.9	1.0
14	0.8	0.0	0.0	0.0	0.1	1.1
17	1.7	1.2	2.4	11.4	1.0	1.1
18	0.2	0.3	0.4	0.6	0.3	0.2
19	0.8	1.0	0.9	0.8	0.1	1.5
20	9.8			3.6		2.2
23	1.7	1.8	3.4		1.7	2.7
24	0.1	1.2	5.1	1.4	1.4	0.0
25	0.2	0.1	0.3	0.0	0.1	0.2
26	1.8	1.9	3.7	1.0	2.2	1.5
27	6.4	5.7	9.6	1.6	10.5	12.7
28-1	2.0	18.9	52.2	0.8	1.9	1.7
28-2	3.6	4.2	8.5	10.2	3.8	0.5
29	1.3	0.9	0.3	0.2	0.8	
33	1.4	9.2	15.6	9.2	10.7	0.0
34	1.3	0.7	0.4	4.9	1.1	3.2
36						
37	0.7	1.0	3.6	1.8	0.9	1.7
38	0.5	0.3	0.4	0.6	0.5	0.0
40						
42	2.9	2.4	1.6	1.4	3.1	3.5
43	0.3	0.0	1.3	1.4	0.1	0.2
45	0.4	0.7	2.6		0.3	0.0
46	1.8	4.6	1.9	0.2	5.1	0.2
48	0.5	0.5	0.3	1.4	0.4	0.8
50	1.2	12.4	12.6	2.2	7.6	9.8
51	7.8	5.0	9.8	1.0	9.9	6.3
52	0.7	0.6	0.7	0.0	0.8	0.7
53	1.5	0.0	0.2	0.8	0.2	0.8
55	0.7	0.7	0.3	0.6	0.7	1.2
56	0.8	0.5	1.1	0.2	0.9	1.1
61	1.0	1.9	1.6	0.6	1.4	1.7
62	1.7	1.6	2.2	2.6	1.7	2.3
63	27.8	32.1	60.9		37.8	23.3

Table 7-1. *Z*-scores for nitrate+nitrite (continued).

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
64	7.1	16.2	22.6	7.3	14.6	6.7
65	0.8	0.5	0.1	0.6	0.5	2.0
66	2.5	2.7	6.2	12.6	1.4	3.3
68	1.0	1.2	1.6	0.2	1.2	1.0
69	0.0	0.2	0.1		0.2	0.2
70	0.9	1.5	0.7	0.6	1.7	1.2
71-1	2.7	1.2	1.6	1.4	0.5	0.8
71-2	4.3	4.1	7.6	1.4	4.0	3.7
72	1.1	1.3	2.9	0.7	1.7	0.0
73	0.5	1.1	0.5	1.6	1.1	3.1
74	0.7	1.5	3.7	9.2	0.3	1.2
75	1.1	1.7	3.2	0.0	1.8	6.4

Table 7-2. *Z*-scores for nitrate analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	0.2	2.1	1.1	3.7	4.6	0.6
2						
3	0	0.1	1	4.3	0.2	0.3
4						
5	0.2	0.1	0.6		0.3	1.1
6						
7	0	0	0.1	1.3	0.2	0
9	0.3	0.2	1.5	0.4	0	1.5
10	1.7	2	3.7	0.7	2.4	0.5
11	1.4	1.2	0.1	2.7	1.2	2.2
13	0.9	0.7	0.5	0.7	0.9	0.8
14	0.7	0.1	0	1.3	0.2	1.1
17	1.4	1.1	2.2	19.3	0.9	1
18	0.2	0.2	0.3	1.7	0.3	0.1
19	0.5	0.8	0.8	0	0	1.1
20						
23	1.4	1.7	3		1.7	1.8
24	0	1	4.5	0.7	1.2	0.2
25	0.2	0.1	0.3	0.7	0.1	0.1
26	1.6	1.7	3.3	0.3	2	1.5
27						
28-1	1.7	16.7	46.2	1.7	1.7	1.4
28-2	3.1	3.7	7.6	17.9	3.4	0.2
29	1.1	0.8	0.3	1.7	0.8	
33	1.1	8.2	14	14.3	10	0.3
34	1.2	0.5	0.5	7.6	1	2.9
36	0.6	0.7	1.2	4.7	0.8	0.1
37	0.4	0.9	3.2	4.3	0.8	1.6
38	0.4	0.3	0.3	2	0.4	0
40						
42	2.6	2.2	1.4	0.7	3	3.1
43	0.3	0	1.1	0.7	0	0.1
45	0.3					0.3
46	1.4	4	1.7	1.7	4.6	0.4
48						
50	1.4	11.1	11.8		7.3	9.8
51	6.7	4.5	8.7	0.3	9.1	4.3
52	0.7	0.6	0.7	1	0.8	0.7
53	1.3	0	0.2	0.3	0.2	0.7
55	0.6	0.6	0.2	1.7	0.8	1
56						
61						
62	1.7	1.6	2.2	2	1.7	2.2
63						

Table 7-2. *Z*-scores for nitrate (continued).

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
64	5.2	14.6	20	0.7	13.9	5.2
65	0.7	0.5	0	0.7	0.4	1.6
66	2.1	2.4	5.5	22.7	1.2	2.9
68	1	1	1.7	0	1.2	0.8
69						
70	0.9	1.2	0.6	1.7	1.7	1.1
71-1	1.9	1.1	1.4	0.7	0.3	1.3
71-2	3.4	3.7	8.5	0.7	3.6	2
72	1.1	1.2	2.6	0	1.7	0.2
73	0.5	1	0.4	3.7	1.1	2.4
74	0.5	1.3	3.3	17	0.1	1.1
75						

Table 7-3. *Z*-scores for nitrite analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	2					0.5
2						
3	1	0	1	1	0	0.5
4	1	0	1	2	1	0
5	0.4	0.2	0.5	0	0.2	0.9
6	2	0	0	1	0	0.5
7	0.2	0.3	0.6	1.2	0.9	0.4
9	1.7	1.3	0.6	1.4	1	1.4
10	2	1	1	1	1	1.5
11	2	0	0	1	0	2
13	1	0	0	1	0	0
14	0	1	0	0	1	1
17	1.2	1.8	1.7	3	1.3	0.9
18	1	1	1	2	1	1
19	2	0	0	0	1	1
20	1	1	1	0	0	0
23	0.7	0.3	0.9		1.3	1.2
24	0	1	0	0	1	0
25	0.5	0.1	0.8	1.6	0	0
26	3	1	0	0	0	2.5
27						
28-1	1	2	3	3	2	0
28-2	0.1	0.3	0.4	1.3	0.8	1.2
29	0	0	0	0	0	0
33	5	6	6	7	6	1.5
34	10	7.2	5.5	7.3	6.7	3.6
36	2	2	2	1	1	1.5
37	4	1	0	0	1	2
38	0	0	1	1	0	0
40						
42	3	3	1	1	3	1.5
43	0.6	0.8	0.1	0.2	0.8	0.8
45	0.2					2.8
46	2	1	0.8	0	2	1.5
48						
50	19	8	22	17	15	15
51	1	0	1	0	3	5.5
52	1	0	0	1	0	1
53	1	1	1	1	1	0.5
55	1	0	1	1	0	0
56						
61	1	0	0	0	0	0.5
62	8.6	9.2	10.4	11.2	8.6	2.5
63	9					6

Table 7-3. *Z*-scores for nitrite (continued).

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
64	35	18.7	1	42.5	18.7	1.1
65	2	3	3	3	2	0.5
66	3	3	3	4	2	1
68	1	1	5	5	4	0
69						
70	0.6	0.7	2.2	1.6	1.4	0.8
71-1	16	1	1	1	1	15
71-2	11	2	2	1	0	7
72	0.4	0.6	0.8	0.4	0.9	0.8
73	1	1	1	1	0	0.5
74	1	1	0	0	1	1
75	2.3	1.2	2	2	2.1	2.4

Table 7-4. *Z*-scores for phosphate analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	0.4	2.2	1.2	0.7	0.8	1
2	0.6	1	1	0.3	1.2	1
3	1.4	1.2	0.6	0.3	1.2	1.7
4	3	4	4.6	0.7	2.8	0.3
5	1.1	1.8	2.7		1.5	0.6
6	0.2	0	0.2	0.7	0.2	0
7	0.2	0.2	0.8	0	0.2	0.3
9	1.7	2.9	4	1.4	3.8	2
10	0.8	1.8	2.2	1.7	1.8	0.3
11	0.6	0.2	0	0	0.5	1.7
13	1.2	1	0.6	0.7	1.2	2
14	2	5.8	2.2	0.3	3.2	1.3
17	0	0.4	0.4	1.8	0.6	0.4
18	1.2	2.2	2	1	2	1.7
19	0.2	0.5	1.2	2	0.2	2.3
20	0.2	0.8	0.8	1.3	0.8	0
23	2	2.8	3		5.2	1.7
24	1.2	1.2	0.2	1	6.5	0.7
25	0.1	0.7	0.6	0.4	0.6	0.2
26	0.2	0.2	0	1.7	0.2	0.7
27	2.2	1.2	1.4	0.3	2.8	0.7
28-1	14.6	19.5	37	0.3	19.5	13.3
28-2	0.2	0.8	1.5	1.4	1.1	1
29	0.2	0.2	0.4	0.7	2.5	0.3
33	2	5.8	10.4	1.7	5.8	2
34	1.4	2.3	3.2	0.9	1.8	2.4
36	0.4	0.2	1.6	0	0	0.3
37	1.2	3.5	4.4	0.3	3	0
38	0.5	0.4	0.1	1.3	0.4	0.8
40	0.2	0.8	2	0.3	0.8	0.3
42	1.2	3.2	0	0.7	4.5	2.7
43	4.4	5.3	8.8	0.4	5.3	5.5
45	1.6	2.2	1.2	5.5	47.4	2.5
46	0	0.8	0.4	1	0	0.7
48	0	0	0.4	0.7	0	0.7
50	11.2	14.5	10.4	9.7	17	12
51	0.4	0.2	0.2	1	2.2	4.3
52	0	0	0.2	0.3	0.2	0.3
53	0.4	0.2	0.2	0.7	0.2	1
55	0.4	0.2	0.2	0.3	0.5	1
56	0.4	0.5	0.2	1	0.2	0.3
61	0.4	1.5	1.4	0.7	1	2.7
62	4.9	5.8	5.6		7.8	12.7
63	0.6	1	0	2.7	1	0.3

Table 7-4. *Z*-scores for phosphate (continued).

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
64	11	24.1	6.5	103.2	1.9	16.3
65	1.3	1.6	1.5	1.8	1.6	1.5
66	0.2	1	0.6	1.3	1	1
68	2	2.5	2	1.7	2	0
69	0.2	0.5	1		0.5	1.7
70	0.2	0	0	0.7	0	0
71-1	3.8	1	2	1	3.2	6.3
71-2	1.6	0	4	1	0.8	0.7
72	3.2	4	2.4	0.4	4	3.3
73	1.9	1.8	0.8	0	1.8	1.1
74	0.4	0.8	1	0.3	0.5	0.3
75	4.1	4.8	2.7	0.5	5	3

Table 7-5. *Z*-scores for silicate analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	5.5	10.7	4.5	1.4	8.5	15.1
2	0.4	0.7	0.7	0.6	0.6	0
3	0.2	0.2	0.1	1.8	0.4	0.3
4	0.1	0.2	0.1	0.3	0	0.4
5	0.2	0	0.4	0.8	0	1.5
6	0.3	0.3	0.3	8.8	0.6	2.3
7	0.2	0.4	0.1	0.3	0.3	0.5
9	0.6	0.4	1.3	8.7	0.1	0.1
10	0.7	1.1	1.2	1	1.1	0.6
11						
13						
14	1.3	2.3	0.7	0.8	2.5	3
17	0.7	1.5	0.4	2.1	0.7	0.8
18	1.7	2.9	2.1	0.3	3.3	2.5
19	0.6	1.3	0.7	0.4	1.4	0.7
20	0.1	0.5	2.3	1.4	0.3	0.1
23	1.8	2.6	1.8	0.9	2.7	2.3
24	2.4	5	3	3.8	5.5	4.6
25	0.4	0.4	0.3	0.9	0.4	0.8
26	0.1	0	0.1	1.7	0.3	0.7
27	1	3.4	0.7	9.4	3.4	1.4
28-1	4.5	10.2	6.1	0.1	0.5	0.1
28-2	4.7	7.4	7.7	3.5	7.3	34.5
29	0	0.3	0.7	0.6	0	0.6
33	0.3	0.7	0.1	0.4	0.6	0.1
34	1.7	31.4	4.5	0.1	2.7	1.1
36	1.3	1.4	0.2	4	1.6	3.8
37	1.1	0.9	0.7	1.7	1.8	1.6
38	0.8	1.2	0.7	0.4	1.1	0.7
40						
42	4.6	8.6	2	0.8	8.8	5.7
43	1.3	2.5	1.6	1	2.4	0.9
45	2	0.9	1.5	1	1.2	2
46	0.3	0	0.1	0.1	0.6	1.1
48	1.1	1.5	0.5	0.1	1.1	0.1
50	8.4	7.5	15.6	1.9	0.4	7.7
51	1.2	2.9	1.1	3	1.4	1.5
52	0.5	1.2	0.8	1.4	1.2	1.1
53	1.2	1.7	1.8	10.5	2.1	3.8
55	0	0.1	0.2	0.1	0.1	0.5
56	0.3	0.7	0.5	0.3	0.8	0.6
61	1.9	3	2	0.7	2.8	2.7
62	4.4	7.9	6	7.8	7.3	4.7
63	0.9	1.1	0.4	3.4	0.7	1.4

Table 7-5. *Z*-scores for silicate (continued).

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
64	16.8	26.9	20.7	3.8	28	22.7
65	0.4	0.9	0.7	2.9	0.9	0.5
66	2	4.1	2.9	1.6	5.6	2
68	1.1	1.8	1.3	2.9	1.3	1.6
69	1.2	1.5	1.4	0.3	1.9	0.7
70	0.9	1.4	0.5	0	1.4	1.2
71-1						
71-2	0.4	3.1	0.2	4.3	0.6	1.2
72	3.7	6.4	5	0.3	7	3.8
73	3.8	5	1.7	1.3	5.2	6.5
74	2.1	3.2	1.6	6.7	3.3	3.9
75	0.8	1.1	0.8	1.6	1.1	0.1

Table 7-6. Combined *Z*-scores for phosphate and nitrate+nitrite analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	0.3	2.4	1.2	1.0	3.0	0.9
2	0.7	0.9	0.7	0.9	1.2	0.8
3	0.7	0.7	0.9	1.2	0.8	1.0
4	1.8	2.4	3.1	1.0	2.0	0.3
5	0.7	1.0	1.7		1.0	1.1
6	0.2	0.0	0.5	0.7	0.2	0.0
7	0.2	0.1	0.5	0.1	0.3	0.2
9	1.0	1.6	2.9	1.1	2.0	1.8
10*	1.3	1.9	3.0	1.2	2.1	0.4
11	1.0	0.8	0.0	0.3	0.9	2.1
13	1.1	0.9	0.6	1.0	1.1	1.5
14	1.4	2.9	1.1	0.2	1.7	1.2
17	0.9	0.8	1.4	6.6	0.8	0.8
18	0.7	1.3	1.2	0.8	1.2	1.0
19	0.5	0.8	1.1	1.4	0.2	1.9
20	5.0			2.5		1.1
23	1.9	2.3	3.2		3.5	2.2
24	0.7	1.2	2.7	1.2	4.0	0.4
25	0.2	0.4	0.5	0.2	0.4	0.2
26	1.0	1.1	1.9	1.4	1.2	1.1
27	4.3	3.5	5.5	1.0	6.7	6.7
28-1	8.3	19.2	44.6	0.6	10.7	7.5
28-2	1.9	2.5	5.0	5.8	2.5	0.8
29	0.8	0.6	0.4	0.5	1.7	
33	1.7	7.5	13.0	5.5	8.3	1.0
34	1.4	1.5	1.8	2.9	1.5	2.8
36*	0.5	0.5	1.4	2.4	0.4	0.2
37	1.0	2.3	4.0	1.1	2.0	0.9
38	0.5	0.4	0.3	1.0	0.5	0.4
40						
42	2.1	2.8	0.8	1.1	3.8	3.1
43	2.4	2.7	5.1	0.9	2.7	2.9
45	1.0	1.5	1.9		23.9	1.3
46	0.9	2.7	1.2	0.6	2.6	0.5
48	0.3	0.3	0.4	1.1	0.2	0.8
50	6.2	13.5	11.5	6.0	12.3	10.9
51	4.1	2.6	5.0	1.0	6.1	5.3
52	0.4	0.3	0.5	0.2	0.5	0.5
53	1.0	0.1	0.2	0.8	0.2	0.9
55	0.6	0.5	0.3	0.5	0.6	1.1

Table 7-6. Combined *Z*-scores for phosphate and nitrate+nitrite analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
56	0.6	0.5	0.7	0.6	0.6	0.7
61	0.7	1.7	1.5	0.7	1.2	2.2
62	3.3	3.7	3.9		4.8	7.5
63	14.2	16.6	30.5		19.4	11.8
64	9.1	20.2	14.6	55.3	8.3	11.5
65	1.1	1.1	0.8	1.2	1.1	1.8
66	1.4	1.9	3.4	7.0	1.2	2.2
68	1.5	1.9	1.8	1.0	1.6	0.5
69	0.1	0.4	0.6		0.4	1.0
70	0.6	0.8	0.4	0.7	0.9	0.6
71-1	3.3	1.1	1.8	1.2	1.9	3.6
71-2	3.0	2.1	5.8	1.2	2.4	2.2
72	2.2	2.7	2.7	0.6	2.9	1.7
73	1.2	1.5	0.7	0.8	1.5	2.1
74	0.6	1.2	2.4	4.8	0.4	0.8
75	2.6	3.3	3.0	0.3	3.4	4.7

*Z-score calculated using nitrate instead of nitrate+nitrite.

Table 7-7. Combined *Z*-scores for phosphate, nitrate+nitrite, and silicate analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
1	2.0	5.1	2.3	1.1	4.8	5.6
2	0.6	0.8	0.7	0.8	1.0	0.5
3	0.5	0.5	0.6	1.4	0.6	0.7
4	1.2	1.6	2.1	0.7	1.3	0.3
5	0.5	0.6	1.3		0.6	1.2
6	0.2	0.1	0.4	3.4	0.3	0.8
7	0.2	0.2	0.3	0.2	0.3	0.3
9	0.9	1.2	2.3	3.6	1.3	1.2
10*	1.1	1.6	2.4	1.1	1.8	0.5
11						
13						
14	1.4	2.7	1.0	0.4	1.9	1.8
17	0.8	1.0	1.1	5.1	0.8	0.8
18	1.0	1.8	1.5	0.6	1.9	1.5
19	0.5	0.9	0.9	1.1	0.6	1.5
20	3.4			2.1		0.8
23	1.8	2.4	2.7		3.2	2.2
24	1.2	2.5	2.8	2.1	4.5	1.8
25	0.2	0.4	0.4	0.4	0.4	0.4
26	0.7	0.7	1.3	1.5	0.9	1.0
27	3.2	3.4	3.9	3.8	5.6	4.9
28-1	7.0	16.2	31.8	0.4	7.3	5.0
28-2	2.8	4.1	5.9	5.0	4.1	12.0
29	0.5	0.5	0.5	0.5	1.1	
33	1.2	5.2	8.7	3.8	5.7	0.7
34	1.5	11.5	2.7	2.0	1.9	2.2
36*	0.8	0.8	1.0	2.9	0.8	1.4
37	1.0	1.8	2.9	1.3	1.9	1.1
38	0.6	0.6	0.4	0.8	0.7	0.5
40						
42	2.9	4.7	1.2	1.0	5.5	4.0
43	2.0	2.6	3.9	0.9	2.6	2.2
45	1.3	1.3	1.8		16.3	1.5
46	0.7	1.8	0.8	0.4	1.9	0.7
48	0.5	0.7	0.4	0.7	0.5	0.5
50	6.9	11.5	12.9	4.6	8.3	9.8
51	3.1	2.7	3.7	1.7	4.5	4.0
52	0.4	0.6	0.6	0.6	0.7	0.7
53	1.0	0.6	0.7	4.0	0.8	1.9
55	0.4	0.3	0.2	0.3	0.4	0.9

Table 7-7. Combined *Z*-scores for phosphate, nitrate+nitrite, and silicate analyses.

Lab	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
56	0.5	0.6	0.6	0.5	0.6	0.7
61	1.1	2.1	1.7	0.7	1.7	2.4
62	3.7	5.1	4.6		5.6	6.6
63	9.8	11.4	20.4		13.2	8.3
64	11.6	22.4	16.6	38.1	14.8	15.2
65	0.8	1.0	0.8	1.8	1.0	1.3
66	1.6	2.6	3.2	5.2	2.7	2.1
68	1.4	1.8	1.6	1.6	1.5	0.9
69	0.5	0.7	0.8		0.9	0.9
70	0.7	1.0	0.4	0.4	1.0	0.8
71-1						
71-2	2.1	2.4	3.9	2.2	1.8	1.9
72	2.7	3.9	3.4	0.5	4.2	2.4
73	2.1	2.6	1.0	1.0	2.7	3.6
74	1.1	1.8	2.1	5.4	1.4	1.8
75	2.0	2.5	2.2	0.7	2.6	3.2

*Z-score calculated using data for nitrate instead of nitrate+nitrite

6. Comparability between results from 2006 and 2008 RMNS I/C studies

Sample4 and Sample6 in the 2006 I/C study and Sample1 in the 2008 I/C study were from the same RMNS batch. Sample4 in the 2008 I/C study was from the same RMNS batch as Sample5 in the 2006 I/C study. Therefore it is possible to check the internal comparability of laboratories that participated in both the 2006 and 2008 I/C studies.

The results for nitrate+nitrite, nitrate, nitrite, phosphate, and silicate from 2006 and 2008 are compared in Tables 8-1 to 8-5 for each laboratory that participated in both I/C studies. The cumulative distributions of the nitrate, phosphate, and silicate concentrations and the differences between 2006 and 2008 are presented in Figures 6–11.

The differences between reported concentrations for Sample4 and Sample6 in 2006 and Sample1 in 2008 were within the consensus standard deviations of each determinant. The differences between the reported concentrations for Sample5 in 2006 and Sample4 in 2008, however, show larger relative differences. This indicates that maintaining comparability might be more difficult when measuring low nutrient concentrations (for example, in surface layers) as compared to higher concentrations.

Table 8-1. Comparison between nitrate+nitrite results from 2006 and 2008 RMNS I/C studies.

Lab #	2006 Sample4+6 µmol kg^{-1}	2008 Sample1 µmol kg^{-1}	Difference µmol kg^{-1}	2006 Sample5 µmol kg^{-1}	2008 Sample4 µmol kg^{-1}	Difference µmol kg^{-1}
1	22.8	22.04	0.76	<0.08	0.13	
2	21.90	22.27	–0.37	0.01	0.00	0.01
3	21.90	21.98	–0.08	0.01	0.17	–0.16
4	23.05	21.79	1.26	0	0.13	–0.13
5	21.549	21.856	–0.307			
6	20.1	21.9	–1.8	0.0	0.1	–0.1
7	21.7	21.9	–0.2	0.06	0.08	–0.02
9	24.50	22.105	2.395	0.24	0.032	0.208
11	22.42	22.5	–0.08	0.01	0.1	–0.09
13	22.17	22.35	–0.18	0.00	0.01	–0.01
14	17.39	22.27	–4.88	0.02	0.07	–0.05
17	23.1502	21.3645	1.7857	0.1185	0.6389	–0.5204
18	22.1	22.05	0.05	0	0.10	–0.1
19	22.7	21.7	1	0.09	0.03	0.06
20	20.18	18.37	1.81		0.25	
24	22.06	22.0	0.06	0.00	0.0	0
25	21.81	22.05	–0.24	0.05	0.068	–0.018
26	21.77	21.32	0.45	0.12	0.02	0.1
27	22.6	19.60	3	0.36	0.15	0.21
28	20.93	21.25	–0.32	1.30	0.11	1.19
29	22.32	22.45	–0.13	0	0.08	–0.08
33	22.02	22.50	–0.48	0.16	0.53	–0.37
34	22.03	22.469	–0.439	0.05	0.314	–0.264
37	21.77	21.73	0.04	0.01	0.16	–0.15
38	21.73	21.79	–0.06	0.05	0.10	–0.05
42	22.23	23.04	–0.81	0.034	0.00	0.034
43	22.520	22.104	0.416	0.000	0.000	0
45	21.8	22.115	–0.315	<0.24	<0.24	
46	20.85	21.3	–0.45	0.06	0.08	–0.02
48	21.8	21.8	0	0.0	0.0	0
50	15.30	21.55	–6.25	0.42	0.18	0.24
53	21.55	21.42	0.13	0.15	0.03	0.12
55	22.52	22.24	0.28	0.03	0.10	–0.07
56	21.89	21.7	0.19	0.01	0.08	–0.07

note: Sample 4+6 means an average of the value from Sample 4 and Sample 6.

Table 8-2. Comparison between nitrate results from 2006 and 2008 RMNS I/C studies.

Lab #	2006 Sample4+6 µmol kg^{-1}	2008 Sample1 µmol kg^{-1}	Difference µmol kg^{-1}	2006 Sample5 µmol kg^{-1}	2008 Sample4 µmol kg^{-1}	Difference µmol kg^{-1}
1	22.4	21.7	0.7	<0.08	0.13	
3	21.57	21.62	–0.05	0	0.15	–0.15
5	21.21	21.511	–0.301			
7	21.3	21.6	–0.3	0.04	0.06	–0.02
9	24.14	21.738	2.402	0.22	0.008	0.212
10	21.4	20.9	0.5	0.0	0.0	0
11	22.07	22.2	–0.13	0.00	0.1	–0.1
13	21.83	21.99	–0.16	0.00	0.00	0
17	22.7936	21.0022	1.7914	0.1084	0.5992	–0.4908
18	21.7	21.70	0	0	0.07	–0.07
19	22.3	21.4	0.9	0.09	0.02	0.07
23	21.9	22.23	–0.33		<0.70	
24	21.57	21.6	–0.03	0.00	0.0	0
25	21.45	21.70	–0.25	0.03	0.042	–0.012
26	21.40	20.94	0.46	0.09	0.01	0.08
28	20.67	20.89	–0.22	1.30	0.07	1.23
29	21.98	22.10	–0.12	0	0.07	–0.07
33	21.66	22.09	–0.43	0.10	0.45	–0.35
34	21.63	22.112	–0.482	0.02	0.249	–0.229
36	21.65	21.37	0.28	0.18	0.16	0.02
37	21.4	21.42	–0.02	0.01	0.15	–0.14
38	21.39	21.44	–0.05	0.05	0.08	–0.03
42	21.9	22.73	–0.83	0.02	0.00	0.02
43	22.204	21.749	0.455	0.000	0.000	0
46	20.51	21.0	–0.49	0.04	0.07	–0.03
50	15.06	21.02	–5.96	0.33		
51	21.09	18.75	2.34	0.14	0.01	0.13
52	21.3	21.89	–0.59	0.00	0.05	–0.05
53	21.20	21.06	0.14	0.13	0.01	0.12
55	22.18	21.88	0.3	0.03	0.07	–0.04

Table 8-3. Comparison between nitrite results from 2006 and 2008 RMNS I/C studies.

Lab #	2006 Sample4+6 µmol kg^{-1}	2008 Sample1 µmol kg^{-1}	Difference µmol kg^{-1}	2006 Sample5 µmol kg^{-1}	2008 Sample4 µmol kg^{-1}	Difference µmol kg^{-1}
1	0.37	0.33	0.04	<0.08	<0.08	
3	0.34	0.36	–0.02	0.01	0.02	–0.01
4	0.35	0.34	0.01	0.02	0.03	–0.01
5	0.35	0.346	0.004		0.010	
7	0.357	0.352	0.005	0.018	0.022	–0.004
9	0.358	0.367	–0.009	0.015	0.024	–0.009
10	0.40	0.37	0.03	0.02	0.00	0.02
11	0.36	0.33	0.03	0.01	0.02	–0.01
13	0.35	0.36	–0.01	0.01	0.02	–0.01
14	0.35	0.35	0	0.01	0.01	0
17	0.3566	0.3623	–0.0057	0.0101	0.0397	–0.0296
18	0.33	0.34	–0.01	0	0.03	–0.03
19	0.34	0.33	0.01	0.00	0.01	–0.01
20	0.27	0.36	–0.09		0.01	
23	0.43	0.357	0.073	0.04	<0.009	
24	0.35	0.35	0	0.02	0.01	0.01
25	0.354	0.355	–0.001	0.022	0.026	–0.004
26	0.37	0.38	–0.01	0.03	0.01	0.02
28	0.26	0.36	–0.1		0.04	
29	0.34	0.35	–0.01	0	0.01	–0.01
33	0.36	0.40	–0.04	0.06	0.08	–0.02
34	0.39	0.450	–0.06	0.07	0.083	–0.013
36	0.34	0.37	–0.03	0.01	0.00	0.01
37	0.37	0.31	0.06	0	0.01	–0.01
38	0.34	0.35	–0.01	0.01	0.02	–0.01
42	0.355	0.32	0.035	0.015	0.00	0.015
43	0.316	0.356	–0.04	0.000	0.012	–0.012
45	0.36	0.352	0.008	<0.06	<0.06	
46	0.34	0.33	0.01	0.02	0.01	0.01
50	0.24	0.54	–0.3	0.09	0.18	–0.09
51	0.42	0.36	0.06	0.04	0.01	0.03
52	0.33	0.34	–0.01	0.00	0.02	–0.02
53	0.35	0.36	–0.01	0.02	0.02	0
55	0.34	0.36	–0.02	0.01	0.02	–0.01

Table 8-4. Comparison between phosphate results from 2006 and 2008 RMNS I/C studies.

Lab #	2006 Sample4+6 µmol kg^{-1}	2008 Sample1 µmol kg^{-1}	Difference µmol kg^{-1}	2006 Sample5 µmol kg^{-1}	2008 Sample4 µmol kg^{-1}	Difference µmol kg^{-1}
1	1.65	1.61	0.04	0.06	0.05	0.01
2	1.60	1.62	–0.02	0.02	0.04	–0.02
3	1.62	1.52	0.1	0.05	0.02	0.03
4	1.62	1.74	–0.12	0.02	0.01	0.01
6	1.52	1.58	–0.06	0.00	0.05	–0.05
7	1.59	1.60	–0.01	0.030	0.03	0
9	1.99	1.674	0.316	0.26	0.073	0.187
10	1.57	1.55	0.02	0.03	0.08	–0.05
11	1.54	1.56	–0.02	0.01	0.03	–0.02
13	1.53	1.53	0	0.00	0.01	–0.01
14	1.56	1.49	0.07	0.065	0.02	0.045
17	1.6485	1.5908	0.0577	0.0261	0.0825	–0.0564
18	1.60	1.65	–0.05	0.04	0.06	–0.02
19	1.58	1.60	–0.02	0.06	0.09	–0.03
20	1.64	1.58	0.06	0.08	0.07	0.01
23	1.67	1.49	0.18	0.04	<0.034	
24	1.72	1.53	0.19	0.06	0.00	0.06
25	1.571	1.585	–0.014	0.020	0.018	0.002
26	1.51	1.58	–0.07	0.02	0.08	–0.06
27	1.41	1.48	–0.07	0.15	0.04	0.11
28	1.52	2.32	–0.8		0.04	
29	1.58	1.58	0	0.01	0.05	–0.04
33	1.56	1.49	0.07	0.09	0.08	0.01
34	1.40	1.659	–0.259	0.06	0.057	0.003
36	1.76	1.61	0.15	0.05	0.03	0.02
37	1.69	1.65	0.04	0.01	0.02	–0.01
38	1.621	1.615	0.006	0.063	0.068	–0.005
40	1.61	1.60	0.01	0.02	0.02	0
42	1.623	1.53	0.093	0.024	0.01	0.014
43	1.733	1.808	–0.075	0.025	0.041	–0.016
45	1.62	1.671	–0.051	0.106	0.196	–0.09
46	1.55	1.59	–0.04	0.01	0.06	–0.05
48	1.61	1.59	0.02	0.05	0.05	0
50	1.41	2.15	–0.74	0.17	0.32	–0.15
51	1.64	1.57	0.07	0.01	0.00	0.01
52	1.55	1.59	–0.04	0.03	0.02	0.01
53	1.55	1.57	–0.02	0.05	0.01	0.04
55	1.60	1.57	0.03	0.02	0.02	0
56	1.58	1.57	0.01	0.05	0.00	0.05

Table 8-5. Comparison between silicate results from 2006 and 2008 RMNS I/C studies.

Lab #	2006 Sample4+6 µmol kg^{-1}	2008 Sample1 µmol kg^{-1}	Difference µmol kg^{-1}	2006 Sample5 µmol kg^{-1}	2008 Sample4 µmol kg^{-1}	Difference µmol kg^{-1}
1	59.8	67.98	–8.18	1.46	1.98	–0.52
3	60.1	59.1	1	2.3	1.4	0.9
4	60.67	59.64	1.03	1.6	1.77	–0.17
5	62.300	59.121	3.179	1.941	1.577	0.364
6	57.7	59.9	–2.2	1.5	3.3	–1.8
7	59.5	59.8	–0.3	1.69	1.67	0.02
9	66.30	60.397	5.903	4.26	0.149	4.111
10	60.0	58.4	1.6	1.5	1.9	–0.4
14	61.53	61.49	0.04	1.82	1.87	–0.05
17	62.1413	58.3539	3.7874	1.7252	1.3478	0.3774
18	59.6	62.1	–2.5	1.77	1.77	0
19	60.6	60.4	0.2	1.87	1.65	0.22
20	58.21	59.25	–1.04	1.50	1.98	–0.48
23	58.1	56.72	1.38	1.25	1.56	–0.31
24	63.2	63.2	0	2.3	2.4	–0.1
25	58.21	58.80	–0.59	1.47	1.55	–0.08
26	58.45	59.60	–1.15	1.10	1.42	–0.32
27	58.6	60.96	–2.36	3.37	0.03	3.34
29	61.90	59.45	2.45	2.05	1.62	0.43
33	58.90	58.97	–0.07	1.81	1.80	0.01
34	59.75	56.769	2.981	1.96	1.731	0.229
36	58.94	61.42	–2.48	2.48	2.44	0.04
37	55.05	61.15	–6.1	0.83	1.41	–0.58
38	58.17	58.17	0	1.64	1.64	0
42	59.44	52.30	7.14	1.99	1.58	0.41
43	58.841	57.459	1.382	2.466	1.900	0.566
45	60	62.521	–2.521	2.0	1.896	0.104
46	55.82	58.95	–3.13	1.59	1.74	–0.15
48	58.5	57.8	0.7	1.6	1.7	–0.1
50	128.13	72.53	55.6		1.37	
51	60.91	61.25	–0.34	1.36	1.18	0.18
52	63.1	60.29	2.81	1.64	1.47	0.17
53	57.40	61.31	–3.91	2.64	3.61	–0.97
55	61.01	59.46	1.55	1.86	1.74	0.12
56	58.72	58.98	–0.26	1.7	1.77	–0.07

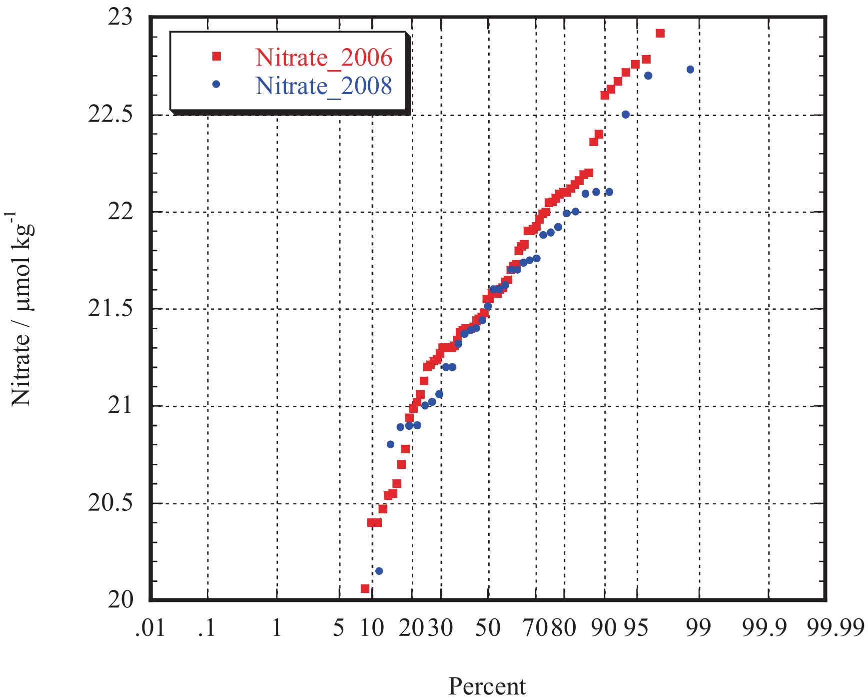

Figure 6. Cumulative distribution of reported nitrate concentrations in 2006 and 2008 I/C studies.

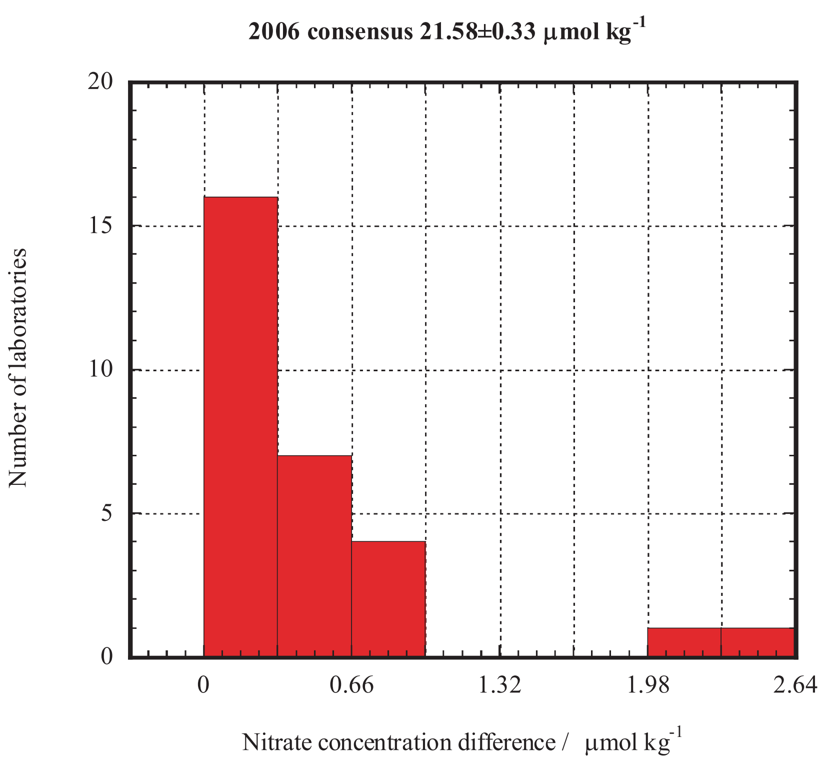

Figure 7. Comparability of nitrate concentrations measured at the same laboratory in

2006 and 2008 I/C studies.

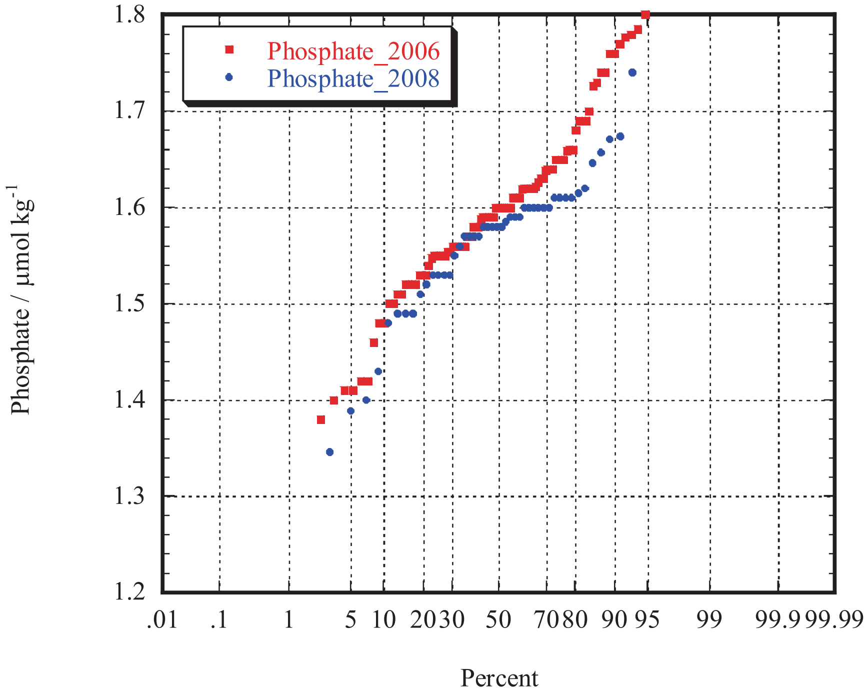

Figure 8. Cumulative distribution of reported phosphate concentrations in 2006 and 2008 I/C studies.

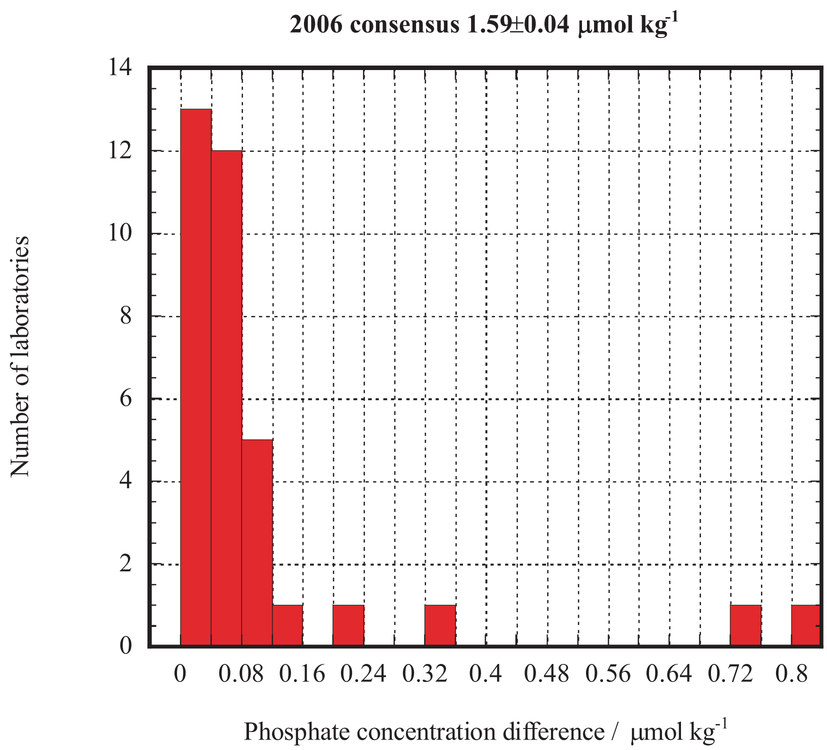

Figure 9. Comparability of phosphate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.

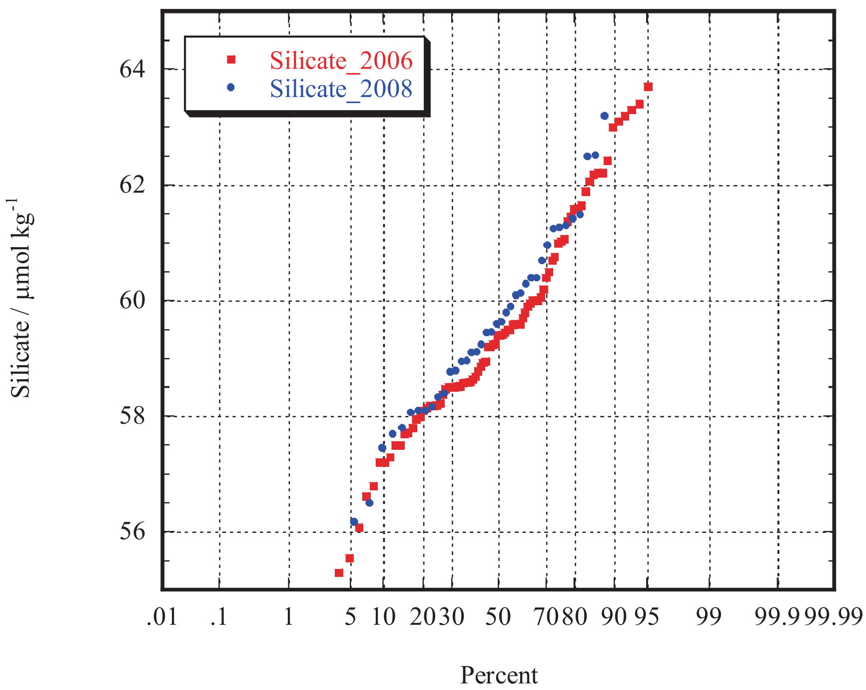

Figure 10. Cumulative distribution of reported silicate concentrations in 2006 and 2008 I/C studies.

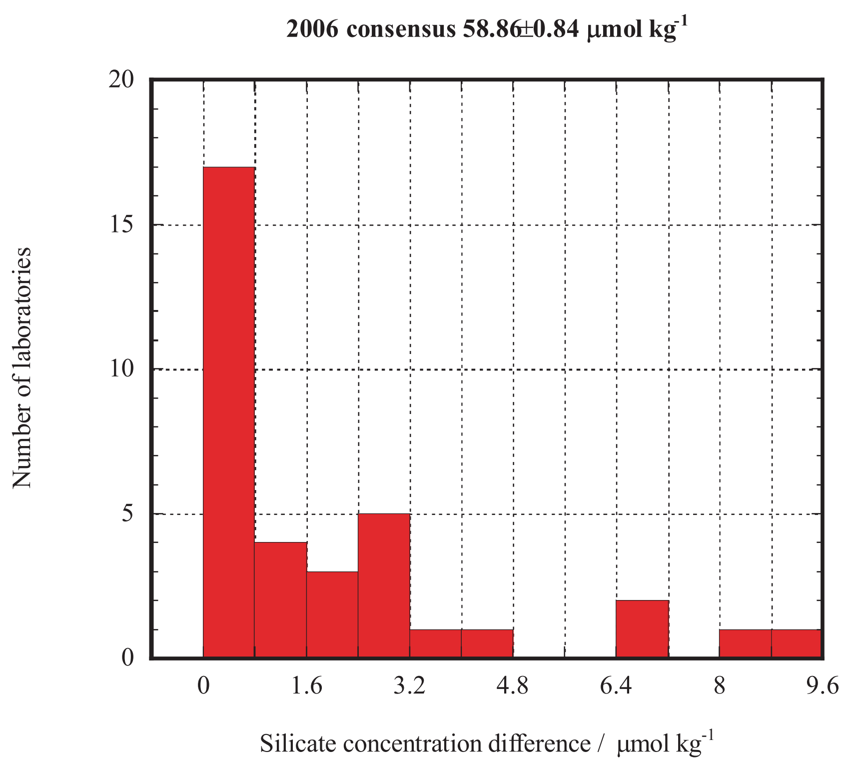

Figure 11. Comparability of silicate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.

7. Discussion and conclusions

In Figures 1–5, the rank scatter plots curves for nitrate, phosphate, and silicate concentrations in the 2008 I/C study, as well those for results from the 2006 study, are the expected S-shaped curves. This indicates that the participating laboratories in both I/C studies has an analytical technique for nutrients that is sufficient to provide data of high comparability. As shown in Figures 7, 9, and 11, the differences between concentrations reported from the same laboratory in 2006 and 2008 for the same RMNS batch demonstrate that most of the laboratories have maintained internal comparability for two years.

Thus, the use of a common reference material and the adoption of an internationally agreed-upon nutrient scale system would increase comparability among laboratories worldwide, and the use of a certified reference material would establish traceability, based on the current high level of analytical performance at participating laboratories.

However, we see a problem of non-linearity of the instruments at the participating laboratories in 2008 similar to that observed in the 2006 I/C study. This problem of non-linearity should be investigated and discussed within the oceanographic community to improve comparability for the full range of nutrient concentrations.

Silicate results showed lower comparability, with relatively larger consensus standard deviations compared to those for nitrate and phosphate. The reasons for this are being examined by Karel Bakker at the Royal Netherlands Institute for Sea Research (NIOZ), and the results will be presented elsewhere in the near future.

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