1. Introduction

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

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

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

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

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

2. Samples

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

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

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

2.2 Selection of determinands

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

2.3 Sample homogeneity

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

Table 1 Homogeneity of sample #2 and analytical precision

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

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

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

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

3. Participants and response

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

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

Table 2 Summary of responses from participants

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

4. Statistical treatment

4.1 Raw means, medians, and standard deviations

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

4.2 Robust statistics

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

4.3 Consensus means, medians, and standard deviations

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

4.4 Calculation of *Z*-scores

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

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

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

5. Results

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

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

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

5.1 Ranked scatter plots of the results

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

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

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

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

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

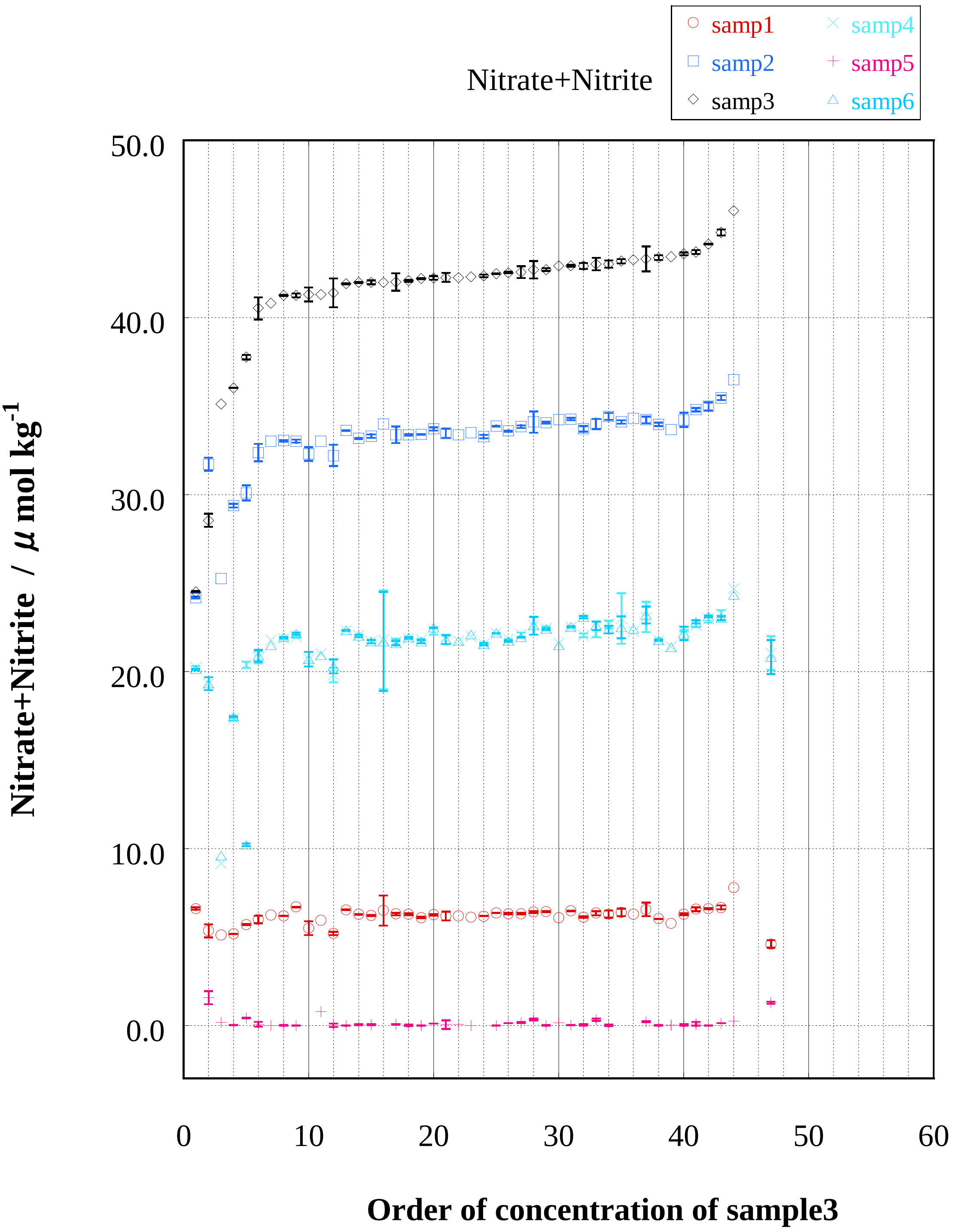

Figure 1 Ranked nitrate+nitrite results for all samples: Reported concentrations were sorted using concentration of sample3.

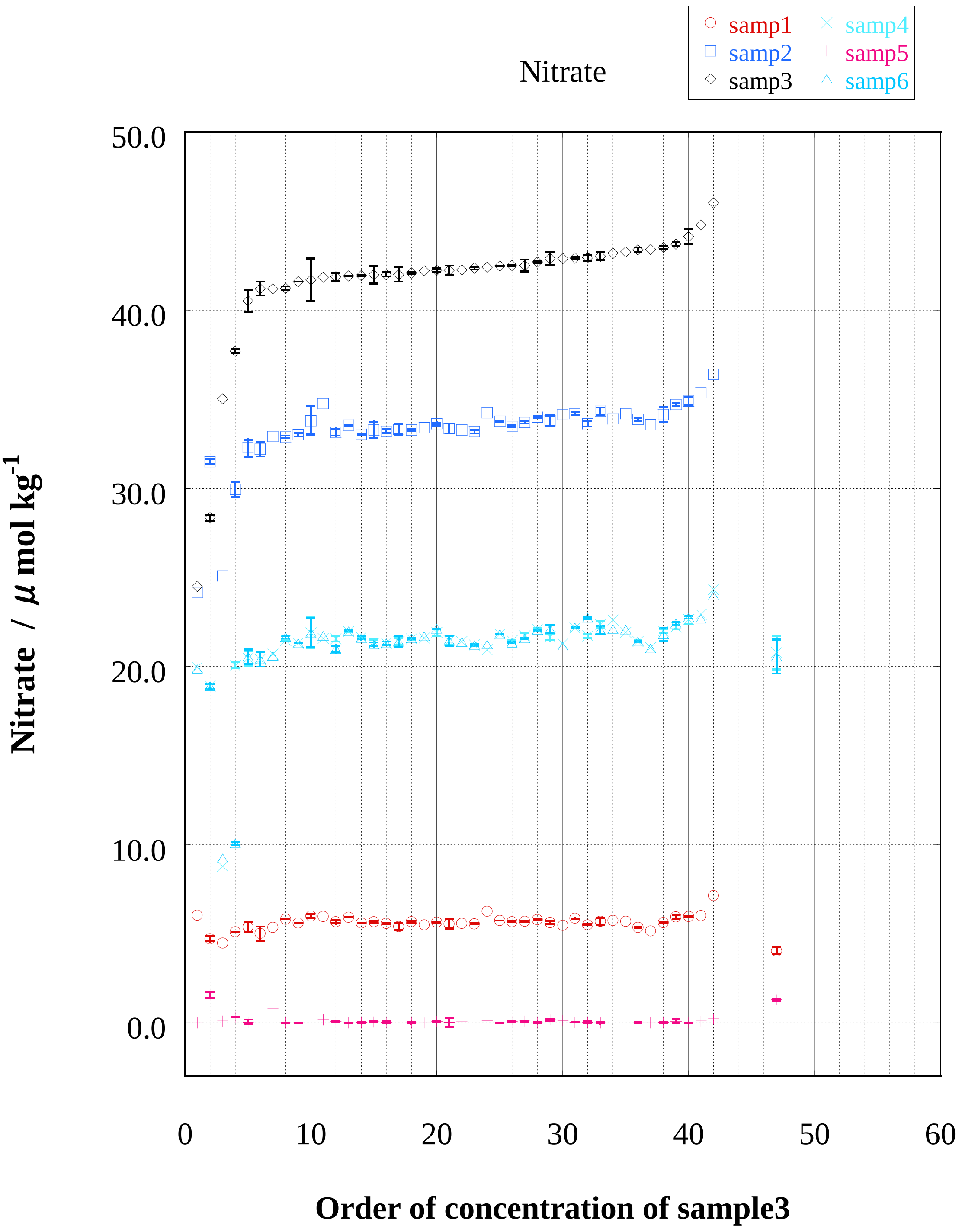

Figure 2 Ranked nitrate results for all samples: Reported concentrations were sorted using concentration of sample3

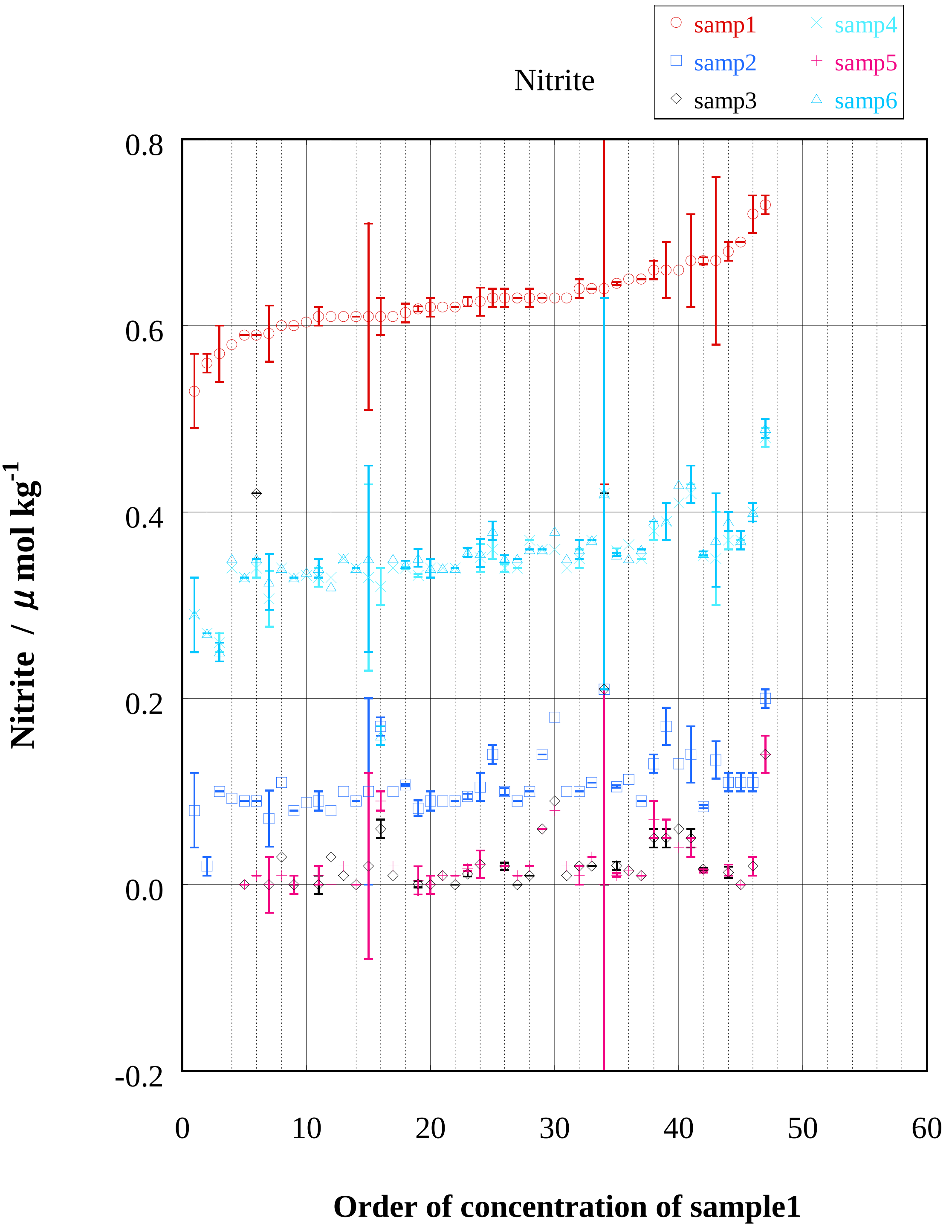

Figure 3 Ranked nitrite results for all samples: Reported concentrations were sorted using concentration of sample1

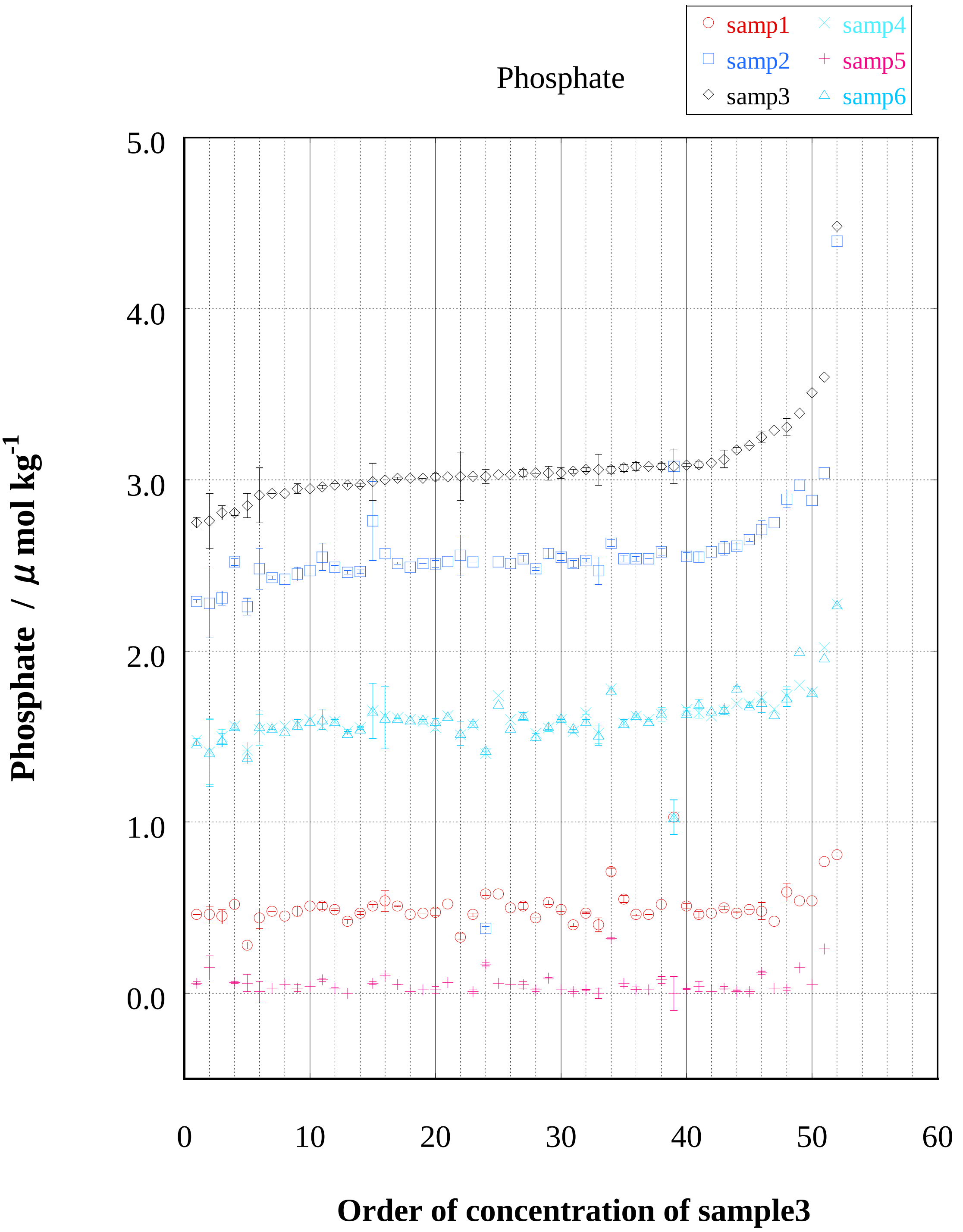

Figure 4 Ranked phosphate results for all samples: Reported concentrations were sorted using concentration of sample3

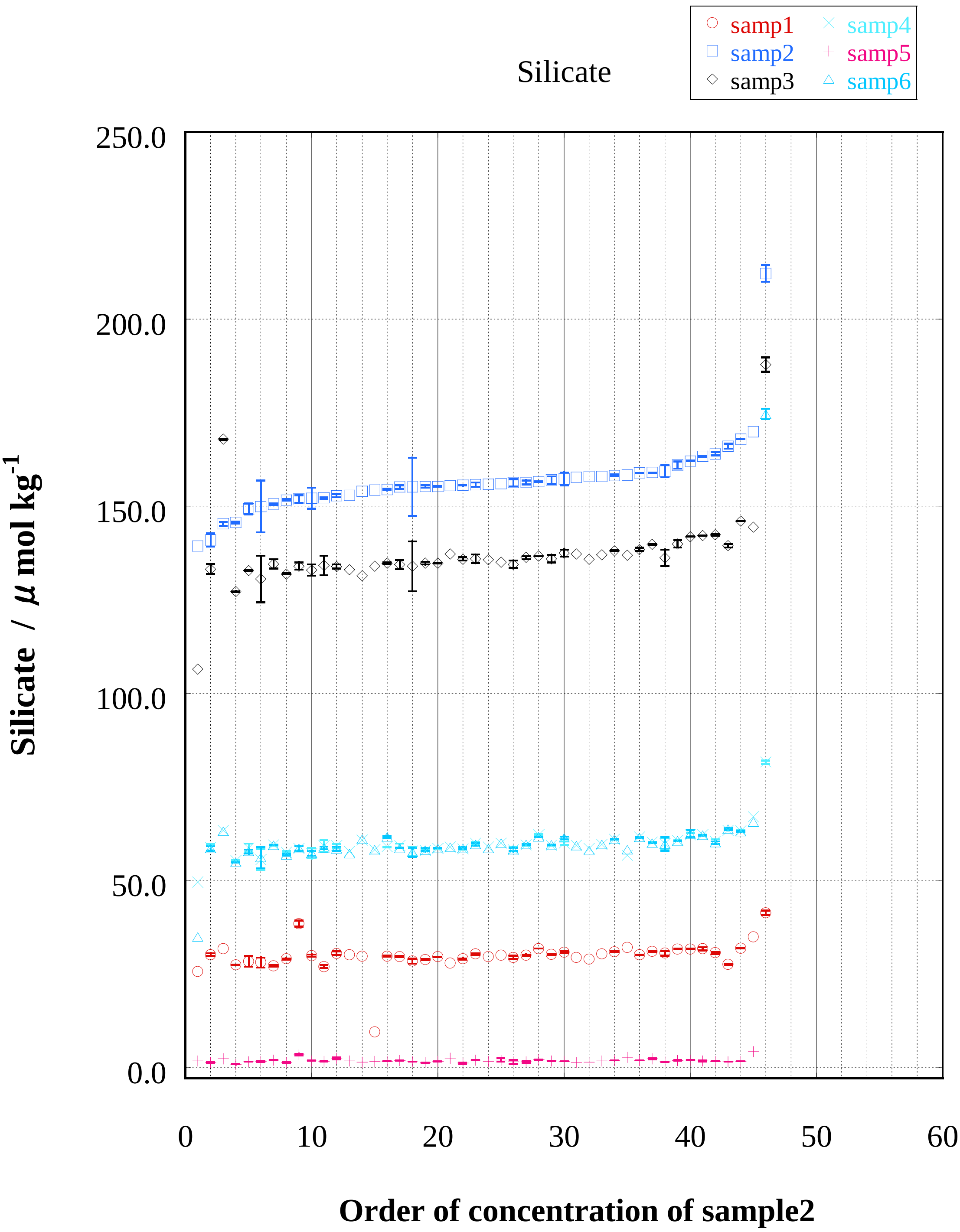

Figure 5 Ranked silicate results for all samples: Reported concentrations were sorted using concentration of sample2

5.2 Consensus medians, means, and standard deviations

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

5.5 *Z*-scores

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

Table 7-1 Z-score for nitrate+nitrite

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

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

Table 7-2 Z-score for nitrate

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

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

Table 7-3 Z-score for nitrite

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

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

Table 7-4 Z-score for phosphate

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

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

Table 7-5 Z-score for silicate

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

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

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

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

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

Note: * means nitrate used instead of nitrate+nitrite

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

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

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

Note: * means nitrate used instead of nitrate+nitrite

6. Conclusions

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

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

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

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

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

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