

## **Appendix I**

### **Participating Laboratories**



**Table A1.** List of participants.

Lab #	Name	Affiliation	Country
1	Nurit Kress	National Institute of Oceanography, Israel Oceanographic and Limnological Research	Israel
2	Atsushi Hirayama	Oceanographical Division, Maizuru Marine Observatory	Japan
3	Susan Becker	Scripps Institution of Oceanography, University of California	USA
4	Jia-Zhong Zhang	Ocean Chemistry Division, Atlantic Oceanographic and Meteorological Laboratory (AOML), National Oceanic and Atmospheric Administration (NOAA)	USA
5	Minhan Dai	State Key Laboratory of Marine Environmental Science, Xiamen University	China
6	David J. Hydes	National Oceanography Centre	United Kingdom
7	Roger Kerouel	Department of DYNECO/Pelagos, Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER)	France
8	—	—	—
9	Cristopher Schmidt	Geochemical and Environmental Research Group, Texas A&M University	USA
10	Hiromi Kasai	Hokkaido National Fisheries Research Institute, Japan Fisheries Research Agency	Japan
11	Hiroyuki Inoue	Oceanographic Division, Nagasaki Marine Observatory	Japan
12	—	—	—
13	Masamitsu Kumagai	Marine Division, Hakodate Marine Observatory	Japan
14	E. Malcolm S. Woodward	Plymouth Marine Laboratory	United Kingdom
15	—	—	—
16	—	—	—
17	Monika Schütt	Institute of Biogeochemistry and Marine Chemistry, University of Hamburg	Germany
18	Agnès Youénou	Department of Dyneco/Pelagos, Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER)	France
19	Olivier Pierre-Duplessix	Laboratoire Environnement Ressources de Normandie (LERN), Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER)	France
20	Theresa M. Shammon	Department of Local Government and the Environment, Isle of Man Government Laboratory	British Isles

**Table A1. List of participants (continued)**

<b>Lab #</b>	<b>Name</b>	<b>Affiliation</b>	<b>Country</b>
21	—	—	—
22	—	—	—
23	Thierry Moutin Olivier Grosso	Laboratoire d'Océanographie Physique et Biogéochimique	France
24	Gwo-Ching Gong	Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University	Taiwan
25	Jan van Ooijen	Royal Netherlands Institute for Sea Research (NIOZ)	the Netherlands
26	Hitoshi Mitsuda	Laboratory for Instrumentation and Analysis, The General Environmental Technos Co., Ltd. (KANSO TECHNOS)	Japan
27	Paul Worsfold	School of Earth, Ocean & Environmental Sciences, University of Plymouth	United Kingdom
28-1	Clemens Engelke	Scottish Environment Protection Agency, Marine Chemistry	United Kingdom
28-2	Judy Dobson	Scottish Environment Protection Agency, Marine Chemistry	United Kingdom
29	Yuzo Ishida	Global Environment and Marine Department, Japan Meteorological Agency	Japan
30	—	—	—
31	—	—	—
32	—	—	—
33	Jeff Anning	Department of Fisheries and Oceans, Bedford Institute of Oceanography	Canada
34	Marguerite Blum	Monterey Bay Aquarium Research Institute	USA
35	—	—	—
36	Katherine A. Krogslund	School of Oceanography, University of Washington	USA
37	Toste Tanhua	Leibniz Institute of Marine Sciences, IFM-GEOMAR	Germany
38	Akihiko Murata	Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology (JAMSTEC)	Japan
	Kenichiro Sato	Marine Works Japan (MWJ)	Japan
39	—	—	—
40	Takeshi Yoshimura	Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry	Japan
41	—	—	—
42	Ingela Dahllöf	Department of Marine Ecology, National Environmental Research Institute, Aarhus University	Denmark
43	Chris Payne	Earth and Ocean Sciences Department, University of British Columbia	Canada

**Table A1. List of participants (continued)**

<b>Lab #</b>	<b>Name</b>	<b>Affiliation</b>	<b>Country</b>
44	—	—	—
45	Marc Knockaert	Department of MARCHEM, Management of Unit of the North Sea Mathematical Models, Royal Belgian Institute of Natural Sciences (MUMM)	Belgium
46	Edward Czobik	NSW Department of Environment and Climate Change, New South Wales Government	Australia
47	—	—	—
48	Janet Barwell-Clarke	Department of Fisheries and Oceans Canada, Institute of Ocean Sciences	Canada
49	—	—	—
50	Jun Sun	Key Laboratory of Marine Ecology & Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences	China
51	Jianming Pan	The Second Institute of Oceanography, State Oceanic Administration	China
52	Hiroshi Ogawa	Ocean Research Institute, University of Tokyo	Japan
53	Günther Nausch	Department of Marine Chemistry, Leibniz Institute for Baltic Sea Research	Germany
54	—	—	—
55	Kazuhiro Saito	Oceanographical Division, Kobe Marine Observatory	Japan
56	Linda White	Ocean Science Division, Institute of Ocean Sciences	Canada
57	—	—	—
58	—	—	—
59	—	—	—
60	—	—	—
61	Solveig Olafsdottir	Marine Research Institute	Iceland
62	Malcolm Rose	Marine Laboratory, Fisheries Research Services	United Kingdom
63	Georges Paradis	Marine Science Institute, University of California Santa Barbara	USA
64	Sophie C. Leterme	School of Biology, Flinders University	Australia
65	Hiroaki Saito	Biological Oceanography, Tohoku National Fisheries Research Institute, Fisheries Research Agency	Japan
66	Sieglinde Weigelt-Krenz	BSH Bundesamt für Seeschifffahrt und Hydrographie (Federal Maritime and Hydrographic Agency)	Germany
67-1	—	—	—
67-2	—	—	—

**Table A1. List of participants (continued)**

<b>Lab #</b>	<b>Name</b>	<b>Affiliation</b>	<b>Country</b>
<b>68</b>	François Baurand	Institut de Recherché pour le Développement, Campus Ifremer Technopole de Brest-Iroise	France
<b>69</b>	Magali Duval	Laboratoire Environnement Ressources France d'Aquitaine (LER-AR), Institut Français de Recherché Pour l'Exploitation de la Mer (IFREMER)	France
	Florence d'Amico	Station d'Arcachon, Institut Français de France Recherché pour l'Exploitation de la Mer (IFREMER)	France
<b>70</b>	Dominique Munaron	Laboratoire Environnement Ressources, Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER)	France
<b>71</b>	Patrick Raimbault	Centre d'Océanologie de Marseille - Service d'Observation	France
<b>72</b>	Gary Prove	Environmental Waters Laboratory, Queensland Health Forensic and Scientific Services	Australia
<b>73</b>	Pascal Morin	Marine Chemistry Laboratory, French National Center for Scientific Research (CNRS) and University Pierre et Marie Curie Paris VI and University Bretagne Occidentale	France
<b>74</b>	Stephen C. Coverly	SEAL Analytical GmbH	Germany
<b>75</b>	Claire Mahaffey	Department of Earth and Ocean Science, University of Liverpool	United Kingdom

**Table A2.** Cross reference for Lab numbers in 2008, 2006, and 2003 I/C studies.

<b>Lab #</b> <b>(2008; this study)</b>	<b>2006 RMNS Inter-comparison</b> <b>Study</b>	<b>2003 RMNS Inter-comparison</b> <b>Study</b>
<b>1</b>	1	2
<b>2</b>	2	10
<b>3</b>	3	3
<b>4</b>	4	
<b>5</b>	5	1
<b>6</b>	6	
<b>7</b>	7	6
<b>9</b>	9	
<b>10</b>	10	17
<b>11</b>	11	15
<b>—</b>	12	
<b>13</b>	13	5
<b>14</b>	14	
<b>—</b>	15	18
<b>—</b>	16	
<b>17</b>	17	
<b>18</b>	18	11
<b>19</b>	19	
<b>20</b>	20	
<b>23</b>	23	
<b>24</b>	24	
<b>25</b>	25	
<b>26</b>	26	16
<b>27</b>	27	
<b>28-1</b>	28	
<b>28-2</b>		
<b>29</b>	29	9
<b>—</b>	30	
<b>—</b>	31	

**Table A2. Cross reference table of lab # between 2008, 2006, and 2003 I/C (continued)**

<b>Lab #</b> <b>(2008; this study)</b>	<b>2006 RMNS Inter-comparison</b> <b>Study</b>	<b>2003 RMNS Inter-comparison</b> <b>Study</b>
—	32	
<b>33</b>	33	
<b>34</b>	34	
—	35	
<b>36</b>	36	
<b>37</b>	37	
<b>38</b>	38	13
—	39	
<b>40</b>	40	
<b>42</b>	42	
<b>43</b>	43	
—	44	
<b>45</b>	45	
<b>46</b>	46	
—	47	
<b>48</b>	48	
—	49	
<b>50</b>	50	
<b>51</b>	51	
<b>52</b>	52	7
<b>53</b>	53	
—	54	
<b>55</b>	55	14
<b>56</b>	56	
<b>57</b>		
<b>58</b>		
<b>59</b>		
<b>60</b>		
<b>61</b>		

**Table A2. Cross reference table of lab # between 2008, 2006, and 2003 I/C (continued)**

Lab # (2008; this study)	2006 RMNS Inter-comparison Study	2003 RMNS Inter-comparison Study
62		
63		
64		
65		8
66		
68		
69		
70		
71-1		
71-2		
72		
73		
74		
75		



## Appendix II

### Results reported by participants

Table A3 Nutrient results reported by the participants

Table A4 Ammonia results reported by the participants

Table A5 DOP results reported by the participants

Table A6 DON results reported by the participants

Table A7 DOC results reported by the participants

(Concentrations in Tables A3–A6 are in units of  $\mu\text{mol kg}^{-1}$ )



Table A3 Results reported by the participants

## 2008 RMNS Intercomparison Exercise

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	
<b>1</b>	1	2009	1	5	22	22.04	1.43	2	21.7	2	0.33	0.01	2	1.61	0.05	2	67.98	0.5	2			
	2	2009	1	5	22	28.84	0.95	2	28.84	2	<0.08	5	2.25	0.11	2	76.98	4.1	2				
	3	2009	1	5	22	41.77	1.27	2	41.77	2	<0.08	5	2.86	0.08	2	168.08	0.6	2				
	4	2009	1	5	22	0.13	0.1	2	0.13	2	<0.08	5	0.05	0.005	2	1.98	0.1	2				
	5	2009	1	5	22	28.02	1.35	2	28.02	2	<0.08	5	2.19	0.06	2	74.44	1.5	2				
	6	2009	1	5	22	6.38	0.32	2	5.76	2	0.62	0.02	2	0.52	0.06	2	38.09	2	2			
<b>2</b>	1	2009	1	9	24.6	22.27	0.05	2	9	9	1.62	0.01	2	58.77	0.15	2						
	2	2009	1	9	25.2	30.27	0.07	2	9	9	2.20	0.02	2	64.96	0.16	2						
	3	2009	1	9	25.0	41.48	0.10	2	9	9	2.85	0.02	2	150.12	0.37	2						
	4	2009	1	9	24.5	0.00	0.00	2	9	9	0.04	0.00	2	1.82	0.00	2						
	5	2009	1	9	25.3	30.37	0.07	2	9	9	2.21	0.02	2	65.01	0.16	2						
	6	2009	1	9	24.8	6.36	0.02	2	9	9	0.46	0.00	2	29.94	0.07	2						
<b>3</b>	1	2008	12	10	21.98	2	21.62	2	0.36	2	1.52	2	59.1	2								
	2	2008	12	10	29.85	2	29.82	2	0.03	2	2.11	2	65.5	2								
	3	2008	12	10	41.75	2	41.72	2	0.02	2	2.77	2	152.4	2								
	4	2008	12	10	0.17	2	0.15	2	0.02	2	0.02	2	2	1.4	2							
	5	2008	12	10	29.85	2	29.82	2	0.03	2	2.11	2	65.2	2								
	6	2008	12	10	6.33	2	5.71	2	0.62	2	0.44	2	2	29.8	2							
<b>4</b>	1	2008	10	27	21.79	0.08	2	9	0.34	0.00	2	1.74	0.02	2	59.64	0.46	2					
	2	2008	10	27	29.63	0.13	2	9	0.03	0.00	2	2.32	0.01	2	66.00	0.44	2					
	3	2008	10	27	40.92	0.12	2	9	0.02	0.01	2	3.03	0.01	2	152.88	0.71	2					
	4	2008	10	27	0.13	0.02	2	9	0.03	0.01	2	0.01	0.02	2	1.77	0.10	2					
	5	2008	10	27	29.52	0.06	2	9	0.04	0.00	2	2.27	0.01	2	65.63	0.40	2					
	6	2008	10	27	6.28	0.06	2	9	0.63	0.01	2	0.48	0.02	2	30.17	0.12	2					

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	ERR	Flag
<b>5</b>	1	2008	11	23	24.4	21.856	0.005	2		21.511	0.005	2	0.346	0.014	2	1.646	0.001	2	59.121	0.042	2		
	2	2008	11	23	24.4	29.888	0.046	2		29.859	0.046	2	0.028	0.004	2	2.233	0.007	2	65.736	0.021	2		
	3	2008	11	23	24.4	41.611	0.035	2		41.597	0.035	2	0.015	0.003	2	2.934	0.004	2	154.097	0.187	2		
	4	2008	11	23	24.4	ND	ND	5		ND	ND	5	0.010	0.002	2	ND	ND	5	1.577	0.001	2		
	5	2008	11	23	24.4	29.786	0.002	2		29.756	0.002	2	0.028	0.003	2	2.220	0.006	2	65.604	0.014	2		
	6	2008	11	23	24.4	6.124	0.062	2		5.512	0.062	2	0.612	0.007	2	0.473	0.000	2	29.132	0.010	2		
<b>6</b>	1	2008	12	23	22	21.9	0.11	2		N/A	9	0.37	0.02	2	1.58	0.01	2	59.9	1.01	2			
	2	2008	12	23	22	29.9	0.21	2		N/A	9	0.03	0.01	2	2.16	0.01	2	66.1	1.00	2			
	3	2008	12	23	22	41.6	0.17	2		N/A	9	0.01	0.00	2	2.79	0.01	2	153.8	1.73	2			
	4	2008	12	23	22	0.1	0.02	2		N/A	9	0.02	0.01	2	0.05	0.01	2	3.3	0.13	2			
	5	2008	12	23	22	29.9	0.18	2		N/A	9	0.03	0.01	2	2.15	0.01	2	66.2	1.10	2			
	6	2008	12	23	22	6.3	0.03	2		N/A	9	0.64	0.01	2	0.49	0.01	2	31.2	0.50	2			
<b>7</b>	1	2008	12	9		21.9		2															
	2	2008	12	9		29.9		2															
	3	2008	12	9		41.36		2															
	4	2008	12	9		0.08		2															
	5	2008	12	9		29.8		2															
	6	2008	12	9		6.30		2															
<b>8</b>	1	2008	12	10																			
	2	2008	11	25		21	22.105		2														
	3	2008	11	25		30.027		2															
	4	2008	11	25		40.854		2															
	5	2008	11	25		0.032		2															
	6	2008	11	25		29.897		2															
<b>9</b>	1	2008	11	25																			
	2	2008	11	25																			
	3	2008	11	25																			
	4	2008	11	25																			
	5	2008	11	25																			
	6	2008	11	25																			

Table A3 Results reported by the participants (continued)

## 2008 RMNS Intercomparison Exercise

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducit	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	Flag
<b>10</b>	1	2008	11	11	20				9	20.9	0.1	2	0.37	0	2	1.55	0.01	2	58.4	0.1	2	
	2	2008	11	11	20				9	28.9	0.1	2	0.02	0	2	2.09	0.01	2	64.6	0.3	2	
	3	2008	11	11	20				9	40.1	0.1	2	0.00	0	2	2.69	0.01	2	148.5	0.6	2	
	4	2008	11	11	20				9	0.0	0.1	2	0.00	0	2	0.08	0.01	2	1.9	0.2	2	
	5	2008	11	11	20				9	28.9	0.2	2	0.02	0	2	2.09	0.01	2	64.5	0.2	2	
	6	2008	11	11	20				9	5.6	0.1	2	0.66	0	2	0.50	0.01	2	29.6	0.0	2	
<b>11</b>	1	2009	1	9	17.6	22.5	0.1	2	22.2	0.1	2	0.33	0.00	2	1.56	0.01	2					9
	2	2009	1	9	17.6	30.5	0.1	2	30.5	0.1	2	0.03	0.00	2	2.15	0.00	2					9
	3	2009	1	9	17.6	41.4	0.1	2	41.4	0.1	2	0.01	0.00	2	2.80	0.00	2					9
	4	2009	1	9	17.6	0.1	0.1	2	0.1	0.1	2	0.02	0.00	2	0.03	0.01	2					9
	5	2009	1	9	17.6	30.4	0.1	2	30.4	0.1	2	0.03	0.00	2	2.14	0.01	2					9
	6	2009	1	9	17.6	6.6	0.1	2	6.0	0.1	2	0.59	0.00	2	0.44	0.01	2					9
<b>13</b>	1	2008	10	16	0	22.35		2	21.99		2	0.36		2	1.53		2					9
	2	2008	10	16	0	30.27		2	30.25		2	0.03		2	2.12		2					9
	3	2008	10	16	0	41.58		2	41.57		2	0.01		2	2.77		2					9
	4	2008	10	16	0	0.01		2	0.00		2	0.02		2	0.01		2					9
	5	2008	10	16	0	30.29		2	30.26		2	0.03		2	2.11		2					9
	6	2008	10	16	0	6.42		2	5.79		2	0.63		2	0.43		2					9
<b>14</b>	1	2008	12	31	22.2	22.27	0.13	2	21.92		2	0.35	0.00	2	1.49	0.02	2	61.49	0.09	2		
	2	2008	12	31	22.2	29.94	0.00	2	29.92		2	0.02	0.00	2	1.93	0.05	2	68.13	0.08	2		
	3	2008	12	31	22.2	41.39	0.12	2	41.38		2	0.01	0.00	2	2.69	0.02	2	154.97	0.21	2		
	4	2008	12	31	22.2	0.07	0.00	2	0.06		2	0.01	0.00	2	0.02	0.00	2	1.87	0.02	2		
	5	2008	12	31	22.2	29.99	0.02	2	29.97		2	0.02	0.00	2	2.03	0.01	2	68.19	0.02	2		
	6	2008	12	31	22.2	6.43	0.01	2	5.84		2	0.61	0.00	2	0.45	0.02	2	31.54	0.04	2		

Table A3 Results reported by the participants (continued)

2008 RMNS Intercomparison Exercise																							
Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducit	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	ERR	Flag
<b>17</b>	1	2008	10	11		21.3645		2		21.0022		2	0.3623		2	1.5908		2	58.3539		2		
	2	2008	10	11		29.3869		2		29.3388		2	0.0482		2	2.1429		2	64.1251		2		
	3	2008	10	11		40.6360		2		40.6086		2	0.0274		2	2.7799		2	151.2715		2		
	4	2008	10	11		0.6389		2		0.5992		2	0.0397		2	0.0825		2	1.3478		2		
	5	2008	10	11		29.5597		2		29.5168		2	0.0429		2	2.1355		2	64.9005		2		
	6	2008	10	11		6.4373		2		5.8249		2	0.6124		2	0.5028		2	29.5315		2		
<b>18</b>	1	2008	12	26		22.05		2		21.70		2	0.34		2	1.65		2	62.1		2		
	2	2008	12	26		30.05		2		30.01		2	0.04		2	2.25		2	68.8		2		
	3	2008	12	26		41.51		2		41.49		2	0.02		2	2.90		2	160.0		2		
	4	2008	12	26		0.10		2		0.07		2	0.03		2	0.06		2	1.77		2		
	5	2008	12	26		30.06		2		30.03		2	0.04		2	2.24		2	69.0		2		
	6	2008	12	26		6.28		2		5.66		2	0.61		2	0.54		2	31.3		2		
<b>19</b>	1	2008	11	27		20		21.7		21.4		2	0.33		2	1.60		2	60.4		2		
	2	2008	11	27		20		29.5		29.5		2	0.03		2	2.14		2	67.1		2		
	3	2008	11	27		41.1		2		41.1		2	0.01		2	2.74		2	155		2		
	4	2008	11	27		0.03		2		0.02		2	0.01		2	0.09		2	1.65		2		
	5	2008	11	27		30.0		2		29.9		2	0.02		2	2.15		2	67.1		2		
	6	2008	11	27		6.12		2		5.51		2	0.61		2	0.56		2	30.3		2		
<b>20</b>	8	2008	11	24		20		9		9		9			9			9		9		9	
	1	2008	10	22		19.5		18.37		2		9		0.36		2	1.58		2	59.25		2	
	2	2008	10	22		19.5		9		9		9		0.02		2	2.19		2	66.28		2	
	3	2008	10	22		19.5		9		9		9		0.00		2	2.84		2	160.62		2	
	4	2008	10	22		19.5		0.25		2		9		0.01		2	0.07		2	1.98		2	
	5	2008	10	22		19.5		9		9		9		0.03		2	2.19		2	65.33		2	
<b>21</b>	6	2008	10	22		19.5		6.56		2		9		0.63		2	0.49		2	29.86		2	
	7	2009	1	6		19.5		9		9		9		0.05		2	2.62		2	268.62		2	
	8	2009	1	6		19.5		0.31		9		9		0.00		2	0.06		2	2.62		2	

Table A3 Results reported by the participants (continued)

2008 RMNS Intercomparison Exercise																							
Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducit	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	ERR	Flag
<b>23</b>	1	2008	12	23	22	22.6	0.2	2	22.23	0.16	2	0.357	0.004	2	1.49	0.03	2	56.72	0.17	2			
	2	2008	12	23	22	30.73	0.09	2	30.72	0.09	2	0.033	0.001	2	2.05	0.05	2	62.99	0.17	2			
	3	2008	12	23	22	42.43	0.16	2	42.43	0.16	2	0.019	0.02	2	2.65	0.03	2	146.50	0.19	2			
	4	2008	12	23	22	<0.70	5	<0.70	5	<0.009	5	<0.009	5	<0.034	5	1.56	0.01	2					
	5	2008	12	23	22	30.58	0.23	2	30.6	0.3	2	0.017	0.001	2	1.95	0.12	2	62.76	0.10	2			
	6	2008	12	23	22	5.98	0.25	2	5.40	0.25	2	0.605	0.001	2	0.44	0.01	2	28.68	0.01	2			
<b>24</b>	1					22.0		2	21.6		2	0.35		2	1.53		2	63.2		2			
	2					29.4		2	29.4		2	0.02		2	2.11		2	71.0		2			
	3					39.8		2	39.8		2	0.01		2	2.81		2	162.9		2			
	4					0.0		2	0.0		2	0.01		2	0.00		2	2.4		2			
	5					29.4		2	29.4		2	0.02		2	1.90		2	71.3		2			
	6					6.3		2	5.7		2	0.63		2	0.51		2	32.4		2			
<b>25</b>	1	2008	12	10	20.0	22.05		2	21.70		2	0.355		2	1.585		2	58.80		2			
	2	2008	12	10	20.0	29.98		2	29.95		2	0.031		2	2.189		2	65.28		2			
	3	2008	12	10	20.0	41.49		2	41.48		2	0.018		2	2.828		2	151.60		2			
	4	2008	12	10	20.0	0.068		2	0.042		2	0.026		2	0.018		2	1.55		2			
	5	2008	12	10	20.0	29.98		2	29.95		2	0.030		2	2.186		2	65.16		2			
	6	2008	12	10	20.0	6.32		2	5.69		2	0.629		2	0.484		2	30.35		2			
<b>26</b>	1	2008	12	25		21.32		2	20.94		2	0.38		2	1.58		2	59.60		2			
	2	2008	12	25		29.07		2	29.05		2	0.02		2	2.15		2	65.70		2			
	3	2008	12	25		40.25		2	40.24		2	0.01		2	2.80		2	152.48		2			
	4	2008	12	25		0.02		2	0.01		2	0.01		2	0.08		2	1.42		2			
	5	2008	12	25		29.12		2	29.09		2	0.03		2	2.15		2	65.91		2			
	6	2008	12	25		6.12		2	5.44		2	0.68		2	0.51		2	30.34		2			

Table A3 Results reported by the participants (continued)

## 2008 RMNS Intercomparison Exercise

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	Flag
<b>27</b>	1	2009	1	10	16	19.60	0.2	2		9	1.48	0.02	2	60.96	1.5	2						
	2	2009	1	10	16	27.41	1.1	2		9	2.11	0.02	2	69.35	2.2	2						
	3	2009	1	10	16	38.42	0.5	2		9	2.73	0.02	2	155.25	2.1	2						
	4	2009	1	10	16	0.15	0.05	2		9	0.04	0.01	2	0.03	0.01	2						
	5	2009	1	10	16	25.95	0.6	2		9	2.05	0.04	2	69.16	1.6	2						
	6	2009	1	10	16	4.78	0.2	2		9	0.47	0.03	2	30.72	0.9	2						
<b>28-1</b>	1	2009	1	9	22	21.25		2		20.89	0.36	2	2.32		2	66.39		2				
	2	2009	1	9	22	21.59		2		21.54	0.05	2	2.94		2	76.44		2				
	3	2009	1	9	22	57.58		2		57.55	0.04	2	4.65		2	131.75		2				
	4	2009	1	9	22	0.11		2		0.07	0.04	2	0.04		2	1.73		2				
	5	2009	1	9	22	29.24		2		29.18	0.05	2	2.94		2	65.09		2				
	6	2009	1	9	22	6.10		2		5.46	0.63	2	0.89		2	29.88		2				
<b>28-2</b>	1	2008	10	21	20.6302		2		20.2815	0.3487	2	1.6012		2	66.73		2					
	2	2008	10	21	28.0795		2		28.0469	0.0326	2	2.1924		2	73.534		2					
	3	2008	10	21	38.7405		2		38.727	0.0136	2	2.8767		2	179.239		2					
	4	2008	10	21	0.5797		2		0.5568	0.0228	2	-0.0116		2	1.083		2					
	5	2008	10	21	28.5242		2		28.502	0.0223	2	2.2027		2	73.223		2					
	6	2008	10	21	6.2425		2		5.6353	0.607	2	0.4601		2	48.596		2					
<b>29</b>	1	2008	11	8	22.45	0.04	2		22.10	0.03	2	0.35	0.00	2	1.58	0.00	2	59.45	0.04	2		
	2	2008	11	8	30.30	0.02	2		30.27	0.02	2	0.03	0.00	2	2.15	0.00	2	65.38	0.03	2		
	3	2008	11	8	41.30	0.01	2		41.29	0.01	2	0.01	0.00	2	2.78	0.00	2	150.20	0.39	2		
	4	2008	11	8	0.08	0.03	2		0.07	0.03	2	0.01	0.00	2	0.05	0.00	2	1.62	0.07	2		
	5	2008	11	8	30.26	0.04	2		30.23	0.04	2	0.03	0.00	2	2.06	0.03	2	65.56	0.04	2		
	6	2008	11	8	9				9	0.63	0.00	2	0.48	0.00	2	30.27	0.15	2				

Table A3 Results reported by the participants (continued)

	Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	Flag	Flag
<b>33</b>	1	2008	11	5	21.3	22.50	0.23	2		22.09	0.23	2	0.40	0.01	2	1.49	0.02	2	58.97	0.40	2			
	2	2008	11	5	21.3	25.89	0.24	2		25.80	0.24	2	0.09	0.00	2	1.93	0.01	2	66.49	2.32	2			
	3	2008	11	5	21.3	36.56	0.17	2		36.48	0.17	2	0.07	0.00	2	2.28	0.03	2	153.01	0.49	2			
	4	2008	11	5	21.3	0.53	0.02	2		0.45	0.02	2	0.08	0.00	2	0.08	0.01	2	1.80	0.08	2			
	5	2008	11	5	21.3	25.89	0.68	2		25.80	0.68	2	0.09	0.00	2	1.93	0.03	2	66.23	1.26	2			
	6	2008	11	5	21.3	6.30	0.20	2		5.62	0.20	2	0.66	0.01	2	0.55	0.01	2	29.87	0.14	2			
<b>34</b>	1	2009	1	12		22.469		2		22.112		2	0.450		2	1.659		2	56.769		2			
	2	2009	1	12		30.226		2		30.145		2	0.102		2	2.252		2	32.724		2			
	3	2009	1	12		41.251		2		41.200		2	0.065		2	2.958		2	137.071		2			
	4	2009	1	12		0.314		2		0.249		2	0.083		2	0.057		2	1.731		2			
	5	2009	1	12		30.359		2		30.283		2	0.097		2	2.233		2	62.843		2			
	6	2009	1	12		6.678		2		6.103		2	0.703		2	0.562		2	29.327		2			
<b>36</b>	1	2008	10		22		9			21.37		2	0.37		2	1.61		2	61.42		2			
	2	2008	10		22		9			29.56		2	0.05		2	2.15		2	67.24		2			
	3	2008	10		22		9			40.96		2	0.03		2	2.88		2	153.35		2			
	4	2008	10		22		9			0.16		2	0.00		2	0.03		2	2.44		2			
	5	2008	10		22		9			29.55		2	0.04		2	2.16		2	67.29		2			
	6	2008	10		22		9			5.68		2	0.66		2	0.50		2	32.01		2			
<b>37</b>	1	2009	1			21.73	0.33	2		21.42	0.33	2	0.31	0.00	2	1.65	0.03	2	61.15	1.26	2			
	2	2009	1			30.37	0.42	2		30.35	0.42	2	0.02	0.00	2	2.30	0.02	2	66.67	0.61	2			
	3	2009	1			42.50	0.27	2		42.50	0.26	2	0.01	0.01	2	3.02	0.01	2	155.26	0.53	2			
	4	2009	1			0.16	0.02	2		0.15	0.02	2	0.01	0.00	2	0.02	0.00	2	1.41	0.08	2			
	5	2009	1			29.60	0.18	2		29.58	0.18	2	0.02	0.00	2	2.28	0.03	2	67.46	0.28	2			
	6	2009	1			6.50	0.12	2		5.91	0.12	2	0.59	0.01	2	0.49	0.01	2	30.80	0.22	2			

Table A3 Results reported by the participants (continued)

## 2008 RMNS Intercomparison Exercise

	Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	ERR	Flag
<b>38</b>	1	2008				21.79	0.02	2		21.44	0.02	2	0.35	0.00	2	1.615	0.005	2	58.17	0.05	2			
	2	2008				29.77	0.03	2		29.74	0.03	2	0.03	0.00	2	2.178	0.006	2	64.44	0.05	2			
	3	2008				41.28	0.04	2		41.26	0.04	2	0.02	0.00	2	2.794	0.008	2	150.28	0.12	2			
	4	2008				0.10	0.00	2		0.08	0.00	2	0.02	0.00	2	0.068	0.000	2	1.64	0.00	2			
	5	2008				29.77	0.03	2		29.74	0.03	2	0.03	0.00	2	2.174	0.006	2	64.42	0.05	2			
	6	2008				6.30	0.01	2		5.67	0.01	2	0.63	0.00	2	0.513	0.001	2	29.55	0.02	2			
	7	2008				36.73	0.04	2		36.67	0.04	2	0.06	0.00	2	2.550	0.006	2	253.93	0.41	2			
<b>40</b>	1	2008				25.5				9			9			9			1.60	0.02		2	9	
	2	2008				25.5				9			9			9			2.19	0.00		2	9	
	3	2008				25.5				9			9			9			2.90	0.00		2	9	
	4	2008				25.5				9			9			9			0.02	0.01		2	9	
	5	2008				25.5				9			9			9			2.19	0.01		2	9	
	6	2008				25.5				9			9			9			0.50	0.00		2	9	
	7	2008				25.5				9			9			9							9	
<b>42</b>	1	2008				22	23.04	2		22.73		2	0.32			2			1.53			2	2	
	2	2008				22	30.99	2		30.98		2	0.00			2			2.03			2	2	
	3	2008				22	41.88	2		41.87		2	0.00			2			2.80			2	2	
	4	2008				22	0.00	2		0.00		2	0.00			2			0.01			2	2	
	5	2008				22	31.11	2		31.11		2	0.00			2			2.34			2	2	
	6	2008				22	6.72	2		6.13		2	0.60			2			0.41			2	2	
	7	2008				22	33.49	2		33.36		2	0.12			2			3.21			2	2	
<b>43</b>	8	2008				22	9			9			9			9			9			2	9	
	1	2008				22.104	0.200	2		21.749	0.220	2	0.356	0.020		2			1.808	0.050		2	2	
	2	2008				29.917	0.200	2		29.894	0.220	2	0.022	0.020		2			2.371	0.050		2	2	
	3	2008				40.989	0.200	2		40.980	0.220	2	0.009	0.020		2			3.242	0.050		2	2	
	4	2008				0.000	0.020	2		0.000	0.040	2	0.012	0.020		2			0.041	0.020		2	2	
	5	2008				29.917	0.200	2		29.894	0.220	2	0.022	0.020		2			2.371	0.050		2	2	
	6	2008				6.326	0.200	2		5.682	0.220	2	0.645	0.020		2			0.655	0.020		2	2	

Table A3 Results reported by the participants (continued)

2008 RMNS Intercomparison Exercise																							
Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag		
<b>45</b>	1	2008	10	21	22	22.115	2.943	2	21.76	2	0.352	0.050	2	1.671	0.188	2	62.521	17.282	2				
	2	2008	10	21	22	30.242	4.025	2		9	<0.06	5	2.250	0.253	2	66.659	18.424	2					
	3	2008	10	21	22	42.196	5.617	2		9	<0.06	5	2.862	0.322	2	157.76	43.61	2					
	4	2008	10	21	22	<0.24	5			9	<0.06	5	0.196	0.022	2	1.896	0.524	2					
	5	2008	10	21	22	29.829	3.970	2		9	<0.06	5	0.263	0.030	2	66.831	18.472	2					
	6	2008	10	21	22	6.294	0.838	2		5.719	2	0.575	0.082	2	0.565	0.064	2	31.047	8.583	2			
<b>46</b>	1	2008	12	4	21.5	21.3		2	21.0		2	0.33		2	1.59		2	58.95		2			
	2	2008	12	4	21.5	27.9		2	27.9		2	0.02		2	2.13		2	65.75		2			
	3	2008	12	4	21.5	40.8		2		40.8		2	0.002		2	2.78		2	152.9		2		
	4	2008	12	4	21.5	0.08		2	0.07		2	0.01		2	0.06		2	1.74		2			
	5	2008	12	4	21.5	28.0		2		28.0		2	0.01		2	2.16		2	66.20		2		
	6	2008	12	4	21.5	6.33		2	5.73		2	0.60		2	0.51		2	30.53		2			
<b>48</b>	1				22.5	21.8		2		9		9	1.59		2	57.8		2					
	2				22.5	29.7		2		9		9	2.16		2	64.2		2					
	3				22.5	41.3		2		9		9	2.78		2	151.1		2					
	4				22.5	0.0		2		9		9	0.05		2	1.7		2					
	5				22.5	30.1		2		9		9	2.16		2	64.5		2					
	6				22.5	6.2		2		9		9	0.51		2	29.9		2					
<b>50</b>	1	2008	12	3		21.55		2	21.02		2	0.54		2	2.15		2	72.53		2			
	2	2008	12	3		24.45		2	24.34		2	0.11		2	2.74		2	57.87		2			
	3	2008	12	3		37.47		2	37.24		2	0.23		2	3.32		2	99.01		2			
	4	2008	12	3		0.18		2		9		9	0.18		2	0.32		2	1.37		2		
	5	2008	12	3		27.06		2		26.88		2	0.18		2	2.84		2	65.21		2		
	6	2008	12	3		5.13		2	4.20		2	0.93		2	0.85		2	34.11		2			

Table A3 Results reported by the participants (continued)

2008 RMNS Intercomparison Exercise																						
Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducit	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	Flag
<b>51</b>	1				25	19.11	2			18.75	2	0.36	2	1.57	2				61.25	2		
	2				25	27.74	2			27.66	2	0.03	2	2.17	2				68.83	2		
	3				25	38.34	2			38.32	2	0.02	2	2.81	2				156.51	2		
	4				25	0.02	2	0.01		0.01	2	0.01	2	0.00	2				1.18	2		
	5				25	26.20	2			26.14	2	0.06	2	2.07	2				67.05	2		
	6				25	5.54	2			5.02	2	0.52	2	0.36	2				30.73	2		
<b>52</b>	1	2009	1	16	22.3	22.23	0.04	2		21.89	0.04	0.34	0.00	2	1.59	0.00	2		60.29	0.11	2	
	2	2009	1	16	22.3	30.20	0.03	2		30.17	0.03	2	0.03	0.00	2	2.16	0.00	2		66.96	0.14	2
	3	2009	1	16	22.3	41.62	0.09	2		41.61	0.09	2	0.01	0.00	2	2.79	0.01	2		155.59	0.10	2
	4	2009	1	16	22.3	0.07	0.01	2		0.05	0.01	2	0.02	0.00	2	0.02	0.00	2		1.47	0.01	2
	5	2009	1	16	22.3	30.24	0.12	2		30.21	0.12	2	0.03	0.00	2	2.17	0.00	2		66.90	0.30	2
	6	2009	1	16	22.3	6.38	0.02	2		5.77	0.02	2	0.61	0.00	2	0.48	0.00	2		30.54	0.06	2
<b>53</b>	1	2008			21.42		2			21.06		0.36		2	1.57		2		61.31		2	
	2	2008			29.92		2			29.89		0.04		2	2.17		2		67.56		2	
	3	2008			41.46		2			41.44		0.02		2	2.81		2		158.86		2	
	4	2008			0.03		2			0.01		0.02		2	0.01		2		3.61		2	
	5	2008			30.02		2			29.98		0.04		2	2.17		2		67.76		2	
	6	2008			6.21		2			5.56		0.64		2	0.46		2		31.97		2	
<b>55</b>	1	2008	1	6	22.24	0.04	2			21.88	0.04	0.36	0.00	2	1.57	0.01	2		59.46	0.14	2	
	2	2008	1	6	30.22	0.06	2			30.19	0.06	0.03	0.00	2	2.15	0.00	2		65.64	0.08	2	
	3	2008	1	6	41.48	0.03	2			41.46	0.03	0.02	0.00	2	2.79	0.00	2		151.83	0.12	2	
	4	2008	1	6	0.10	0.02	2			0.07	0.02	0.02	0.00	2	0.02	0.00	2		1.74	0.04	2	
	5	2008	1	6	30.23	0.05	2			30.20	0.05	0.03	0.00	2	2.14	0.01	2		65.74	0.08	2	
	6	2008	1	6	6.45	0.01	2			5.82	0.01	0.63	0.00	2	0.46	0.00	2		30.19	0.04	2	

Table A3 Results reported by the participants (continued)

2008 RMNS Intercomparison Exercise

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	
<b>56</b>	1	2009	1	12	18	21.6	2			9	1.57	0.00	2	58.98	0.05	2						
	2	2009	1	12	18	29.1	2			9	2.18	0.01	2	64.96	0.06	2						
	3	2009	1	12	18	40.9	2			9	2.79	0.00	2	150.79	0.03	2						
	4	2009	1	12	18	0.1	2			9	0.00	0.00	2	1.77	0.00	2						
	5	2009	1	12	18	29.4	2			9	2.15	0.01	2	64.75	0.04	2						
	6	2009	1	12	18	6.5	2			9	0.48	0.01	2	29.63	0.05	2						
<b>61</b>	1	2009	1	12	18	21.6	2			9	0.34	2	1.57	2	56.5	2						
	2	2009	1	12	18	29.1	2			9	0.03	2	2.10	2	62.6	2						
	3	2009	1	12	18	40.9	2			9	0.01	2	2.73	2	145.9	2						
	4	2009	1	12	18	0.1	2			9	0.01	2	0.05	2	1.6	2						
	5	2009	1	12	18	29.4	2			9	0.03	2	2.12	2	62.7	2						
	6	2009	1	12	18	6.5	2			9	0.62	2	0.57	2	31.4	2						
<b>62</b>	1	2008	12	4	19	21.334	2			20.898	2	0.436	2	1.346	2	66.299	2					
	2	2008	12	4	19	29.234	2			29.112	2	0.122	2	1.930	2	74.062	2					
	3	2008	12	4	19	40.714	2			40.600	2	0.114	2	2.520	2	173.280	2					
	4	2008	12	4	19	0.201	2			0.079	2	0.122	2	<LOD	5	0.311	2					
	5	2008	12	4	19	29.297	2			29.181	2	0.116	2	1.848	2	73.205	2					
	6	2008	12	4	19	6.026	2			5.346	2	0.680	2	0.108	2	32.482	2					
<b>63</b>	1	2009	1	13	20	11.7	2			9	0.26	2	1.56	2	58.1	2						
	2	2009	1	13	20	15.8	2			9	ND	5	2.12	2	64.6	2						
	3	2009	1	13	20	22.5	2			9	ND	5	2.80	2	151.4	2						
	4	2009	1	13	20	ND	5			9	ND	5	0.11	2	1.1	2						
	5	2009	1	13	20	15.6	2			9	ND	5	2.12	2	64.9	2						
	6	2009	1	13	20	3.5	2			9	0.51	2	0.50	2	29.2	2						

Table A3 Results reported by the participants (continued)

2008 RMNS Intercomparison Exercise																								
Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	ERR	Flag	Flag
<b>64</b>	1	2008	11	14	25	21.68	2	19.355	2	0.000	2	1.042	2	33.333	2									
	2	2008	11	14	25	29.70	2	22.581	2	0.217	2	3.125	2	37.500	2									
	3	2008	11	14	25	48.387	2	48.387	2	0.000	2	3.125	2	81.250	2									
	4	2008	11	14	25	0.435	2	0.000	2	0.435	2	3.125	2	1.042	2									
	5	2008	11	14	25	24.411	2	24.194	2	0.217	2	2.083	2	36.458	2									
	6	2008	11	14	25	7.104	2	6.452	2	0.652	2	0.000	2	17.708	2									
<b>65</b>	1	2008	11	14	25	21.68	2	21.32	2	0.37	2	1.657	2	60.13	2									
	2	2008	11	14	25	29.70	2	29.64	2	0.06	2	2.224	2	66.64	2									
	3	2008	11	14	25	41.41	2	41.38	2	0.04	2	2.875	2	155.05	2									
	4	2008	11	14	25	0.04	2	0.00	2	0.04	2	0.083	2	1.20	2									
	5	2008	11	14	25	29.77	2	29.73	2	0.05	2	2.224	2	66.49	2									
	6	2008	11	14	25	6.06	2	5.43	2	0.64	2	0.536	2	30.22	2									
<b>66</b>	1	2008	12	1	22.5	22.9	2	22.5	2	0.38	2	1.60	2	62.5	2									
	2	2008	12	1	22.0	31.1	2	31.1	2	0.06	2	2.20	2	70.0	2									
	3	2008	12	1	22.0	43.3	2	43.3	2	0.04	2	2.83	2	162.8	2									
	4	2008	12	1	22.0	0.7	2	0.7	2	0.05	2	0.07	2	2.0	2									
	5	2008	12	1	22.5	30.5	2	30.4	2	0.05	2	2.20	2	71.4	2									
	6	2008	12	1	22.5	6.7	2	6.1	2	0.65	2	0.52	2	31.0	2									
	8	2008	12	1	22.5	9	9	9	9	9	9	9	9	9	9									
<b>68</b>	1	2008	12	1	21.5	21.6	2	21.2	2	0.34	2	1.49	2	57.7	2									
	2	2008	12	1	21.5	29.4	2	29.4	2	0.04	2	2.06	2	63.8	2									
	3	2008	12	1	21.5	40.9	2	40.8	2	0.06	2	2.70	2	148.1	2									
	4	2008	12	1	21.5	0.08	2	0.02	2	0.06	2	0.08	2	1.20	2									
	5	2008	12	1	21.5	29.5	2	29.4	2	0.07	2	2.08	2	64.2	2									
	6	2008	12	1	21.5	6.18	2	5.55	2	0.63	2	0.49	2	29.1	2									

Table A3 Results reported by the participants (continued)

## 2008 RMNS Intercomparison Exercise

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	Flag
<b>69</b>	1	2008	12	1	20	21.98		2		9		9	1.58		2	61.27		2				
	2	2008	12	1	20	29.99		2		9		9	2.14		2	67.31		2				
	3	2008	12	1	20	41.36		2		9		9	2.75		2	157.45		2				
	4	2008	12	1	20	<0.49	0.07	5		9		9	<0.10	0.08	5	1.77		2				
	5	2008	12	1	20	30.01		2		9		9	2.14		2	67.57		2				
	6	2008	12	1	20	6.32		2		9		9	0.54		2	30.33		2				
	7	2008	12	1	20					9		9				9		2				
	8	2008	12	1	20					9		9				9		2				
<b>70</b>	1	2008	1222-24	19	22.3		2		22.0		2	0.356		2	1.60		2	58.1		2		
	2	2008	1222-24	19	30.6		2		30.5		2	0.037		2	2.16		2	64.3		2		
	3	2008	1222-24	19	41.6		2		41.6		2	0.032		2	2.80		2	151		2		
	4	2008	1222-24	19	0.10		2		0.07		2	0.026		2	0.008		2	1.72		2		
	5	2008	1222-24	19	30.6		2		30.6		2	0.044		2	2.16		2	64.1		2		
	6	2008	1222-24	19	6.15		2		5.51		2	0.645		2	0.489		2	29.3		2		
	7	2008	1222-24	19	37.1		2		37.0		2	0.079		2	2.57		2	258		2		
	8	2008	1222-24	19						9		9				9		9		9		
<b>71-1</b>	1	2008	11	4	19	20.98		2		20.80		2	0.19		2	1.40		2	9			
	2	2008	11	4	19	29.4		2		29.36		2	0.02		2	2.20		2	9			
	3	2008	11	4	19	40.9		2		40.89		2	0.00		2	2.9		2	9			
	4	2008	11	4	19	0.00		2		0.00		2	0.00		2	0.00		2	9			
	5	2008	11	4	19	29.77		2		29.75		2	0.02		2	2.03		2	9			
	6	2008	11	4	19	6.20		2		5.86		2	0.33		2	0.30		2	9			
	7	2008	11	4	19	36.4		2		36.35		2	0.06		2	2.69		2	9			
	8	2008	11	4	19	0.00		2		0.00		2	0.00		2	0.00		2	9			

Table A3 Results reported by the participants (continued)

## 2008 RMNS Intercomparison Exercise

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	ERR	Flag
71-2	1	2008	11	4	19	20.40		2		20.15		2	0.24		2	1.51		2	60.1		2		
	2	2008	11	4	19	28.11		2		28.06		2	0.05		2	2.16		2	69.0		2		
	3	2008	11	4	19	39.03		2		38.42		2	0.03		2	3.0		2	153.2		2		
	4	2008	11	4	19	0.00		2		0.00		2	0.00		2	0.00		2	2.49		2		
	5	2008	11	4	19	28.43		2		28.41		2	0.03		2	2.13		2	65.0		2		
	6	2008	11	4	19	5.86		2		5.37		2	0.49		2	0.47		2	29.3		2		
	7	2008	11	4	19	9		9		9		9	9		9	9		9	273.3		2		
	8	2008	11	4	19	9		9		9		9	9		9	9		9	2.88		2		
72	1	2008			24	22.4		2		22.1		2	0.346		2	1.43		2	65.2		2		
	2	2008			24	30.5		2		30.5		2	0.0244		2	2.00		2	72.5		2		
	3	2008			24	42.3		2		42.3		2	0.0025		2	2.68		2	170		2		
	4	2008			24	0.0349		2		0.0209		2	0.0140		2	0.0190		2	1.66		2		
	5	2008			24	30.6		2		30.6		2	0.0209		2	2.00		2	72.9		2		
	6	2008			24	6.30		2		5.70		2	0.615		2	0.391		2	32.0		2		
73	1	2008	11	17	20.5	22.18		2		21.84		2	0.34		2	1.684		2	65.3		2		
	2	2008	11	17	20.5	30.42		2		30.38		2	0.04		2	2.23		2	70.98		2		
	3	2008	11	17	20.5	41.55		2		41.53		2	0.02		2	2.84		2	158.4		2		
	4	2008	11	17	20.5	0.15		2		0.13		2	0.02		2	0.03		2	1.96		2		
	5	2008	11	17	20.5	30.36		2		30.33		2	0.03		2	2.23		2	70.98		2		
	6	2008	11	17	20.5	6.67		2		6.029		2	0.64		2	0.522		2	33.47		2		
74	1	2008	12	17	21.73		2			21.39		2	0.34		2	1.61		2	56.18		2		
	2	2008	12	17	29.24		2			29.22		2	0.02		2	2.19		2	62.38		2		
	3	2008	12	17	40.23		2			40.22		2	0.01		2	2.85		2	147.08		2		
	4	2008	12	17	0.53		2			0.53		2	0.01		2	0.02		2	0.51		2		
	5	2008	12	17	29.85		2			29.84		2	0.02		2	2.18		2	62.17		2		
	6	2008	12	17	6.45					5.84		2	0.61		2	0.48		2	27.82		2		

**Table A3 Results reported by the participants (continued)****2008 RMNS Intercomparison Exercise**

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reducut	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	Flag
75																						
1	2009	1	9	16.2	22.40			2		9	0.373		2	1.387		2	58.247		2		2	
2	2009	1	9	16.2	30.67			2		9	0.042		2	1.970		2	64.620		2		2	
3	2009	1	9	16.2	42.39			2		9	0.030		2	2.667		2	149.90		2		2	
4	2009	1	9	16.2	0.07			2		9	0.030		2	0.044		2	1.43		2		2	
5	2009	1	9	16.2	30.64			2		9	0.051		2	1.96		2	64.43		2		2	
6	2009	1	9	16.2	7.07			2		9	0.679		2	0.401		2	29.9		2		2	

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

**Table A4. Ammonia results reported by the participants (continued).**

Lab #	Sample	Ammonia	Error	Nitrite	Error	Nitrate	Error	Nitrate+Nitrite	Error
28-2									
	1	0.8156		0.3487		20.2815		20.6302	
	2	2.3825		0.0326		28.0469		28.0795	
	3	2.1807		0.0136		38.727		38.7405	
	4	1.1964		0.0228		0.5568		0.5797	
	5	2.7496		0.0223		28.502		28.5242	
	6	0.917		0.607		5.6353		6.2425	
33									
	1	0.95	0.03	0.4	0.01	22.09	0.23	22.5	0.23
	2	2.85	0.07	0.09	0	25.8	0.24	25.89	0.24
	3	1.86	0.03	0.07	0	36.48	0.17	36.56	0.17
	4	1.41	0.1	0.08	0	0.45	0.02	0.53	0.02
	5	2.84	0.14	0.09	0	25.8	0.68	25.89	0.68
	6	1.15	0.11	0.66	0.01	5.62	0.2	6.3	0.2
42									
	8	4.84							
45									
	1	0.805	0.255	0.352	0.05	21.76		22.115	2.943
	2	1.813	0.575	<0.06				30.242	4.025
	3	2.344	0.744	<0.06				42.196	5.617
	4	0.653	0.207	<0.06				<0.24	
	5	1.766	0.56	<0.06				29.829	3.97
	6	0.577	0.183	0.575	0.082	5.719		6.294	0.838
46									
	1	0.84		0.33		21		21.3	
	2	2.73		0.02		27.9		27.9	
	3	2.38		0.002		40.8		40.8	
	4	1.3		0.01		0.07		0.08	
	5	3.14		0.01		28		28	
	6	0.95		0.6		5.73		6.33	
51									
	1	1.04		0.36		18.75		19.11	
	2	2.85		0.03		27.66		27.74	
	3	1.72		0.02		38.32		38.34	
	4	1.28		0.01		0.01		0.02	
	5	3.29		0.06		26.14		26.2	
	6	1.35		0.52		5.02		5.54	
66									
	1	1.2		0.38		22.5		22.9	
	2	2.9		0.06		31.1		31.1	
	3	2.3		0.04		43.3		43.3	
	4	1.6		0.05		0.7		0.7	
	5	2.7		0.05		30.4		30.5	
	6	1.3		0.65		6.1		6.7	
	8	5.2							

**Table A4. Ammonia results reported by the participants (continued).**

Lab #	Sample	Ammonia	Error	Nitrite	Error	Nitrate	Error	Nitrate+Nitrite	Error
51									
	1	1.04		0.36		18.75		19.11	
	2	2.85		0.03		27.66		27.74	
	3	1.72		0.02		38.32		38.34	
	4	1.28		0.01		0.01		0.02	
	5	3.29		0.06		26.14		26.2	
	6	1.35		0.52		5.02		5.54	
66									
	1	1.2		0.38		22.5		22.9	
	2	2.9		0.06		31.1		31.1	
	3	2.3		0.04		43.3		43.3	
	4	1.6		0.05		0.7		0.7	
	5	2.7		0.05		30.4		30.5	
	6	1.3		0.65		6.1		6.7	
	8	5.2							
69									
	8	4.74							
70									
	8	3.99							
71-1									
	2	2.52		0.02		29.36		29.4	
	3	1.25		0		40.89		40.9	
	4	1.07		0		0		0	
	7	1.44		0.06		36.35		36.4	
	8	3.93		0		0		0	
72									
	1	0.52		0.346		22.1		22.4	
	2	2.06		0.0244		30.5		30.5	
	3	1.38		0.0025		42.3		42.3	
	4	0.859		0.014		0.0209		0.0349	
	5	2.83		0.0209		30.6		30.6	
	6	0.624		0.615		5.7		6.3	

**Table A5. Dissolved organic phosphate (DOP) results reported by the participants.**  
Concentrations are in  $\mu\text{mol kg}^{-1}$ .

Lab #	Sample	Phosphate	Error	DOP	Error
40	6	0.5	0	0.14	0
	5	2.19	0.01	0.03	0.02
	4	0.02	0.01	0.18	0.02
	3	2.9	0	0.08	0.01
	2	2.19	0	0.03	0.01
	1	1.6	0.02	0.19	0.02
42	2	2.03		2.06	
	3	2.8		2.84	
	4	0.01		0.21	
45	6	0.565	0.064	0.53	0.16
	1	1.671	0.188	1.58	0.47
	2	2.25	0.253	2.09	0.62
	3	2.862	0.322	3.02	0.9
	4	0.196	0.022	0.15	0.04
	5	0.263	0.03	2.21	0.66
66	3	2.83		0.1	
	4	0.07		0	
	2	2.2		0	
71-1	8	0		0.12	
	7	2.69		0.03	
	4	0		0.15	
	3	2.9		0.27	
	2	2.2		0.05	

**Table A6. Dissolved organic nitrogen (DON) results reported by the participants. All concentrations are in  $\mu\text{mol kg}^{-1}$ .**

Lab #	Sample	DON	Error	Nitrite	Error	Nitrate	Error	Nitrite + Nitrate	Error	Ammonia	Error
7	2	2.6		0.033		29.9		29.9		2.93	
	3	2.4		0.016		41.34		41.36		1.97	
	4	3.7		0.022		0.06		0.08		1.1	
42	2	33.73		0		30.98		30.99			
	3	43.12		0		41.87		41.88			
	4	5.44		0		0		0			
45	1	27.1	5.83	0.352	0.05	21.76		22.115	2.943	0.805	0.255
	2	35.06	7.54	<0.06				30.242	4.025	1.813	0.575
	3	46.78	10.06	<0.06				42.196	5.617	2.344	0.744
	4	5.37	1.16	<0.06				<0.24		0.653	0.207
	5	35.16	7.56	<0.06				29.829	3.97	1.766	0.56
	6	11.73	2.52	0.575	0.082	5.719		6.294	0.838	0.577	0.183
66	2	0.8		0.06		31.1		31.1		2.9	
	3	0		0.04		43.3		43.3		2.3	
	4	2.6		0.05		0.7		0.7		1.6	
71-1	2	2.57		0.02		29.36		29.4		2.52	
	3	2.02		0		40.89		40.9		1.25	
	4	4.12		0		0		0		1.07	
	7	1.5		0.06		36.35		36.4		1.44	
	8	4.85		0		0		0		3.93	

**Table A7. Dissolved organic carbon (DOC) results reported by the participants. All concentrations are in  $\mu\text{mol kg}^{-1}$ .**

Lab	Sample	DOC	Error
40			
	1	135.6	1.2
	2	96.5	1.8
	3	80.6	1.5
	4	168.1	1.7
	5	98.9	1.4
	6	161.5	3.5



**Table A4. Ammonia results reported by the participants. All concentrations are  $\mu\text{mol kg}^{-1}$ .**

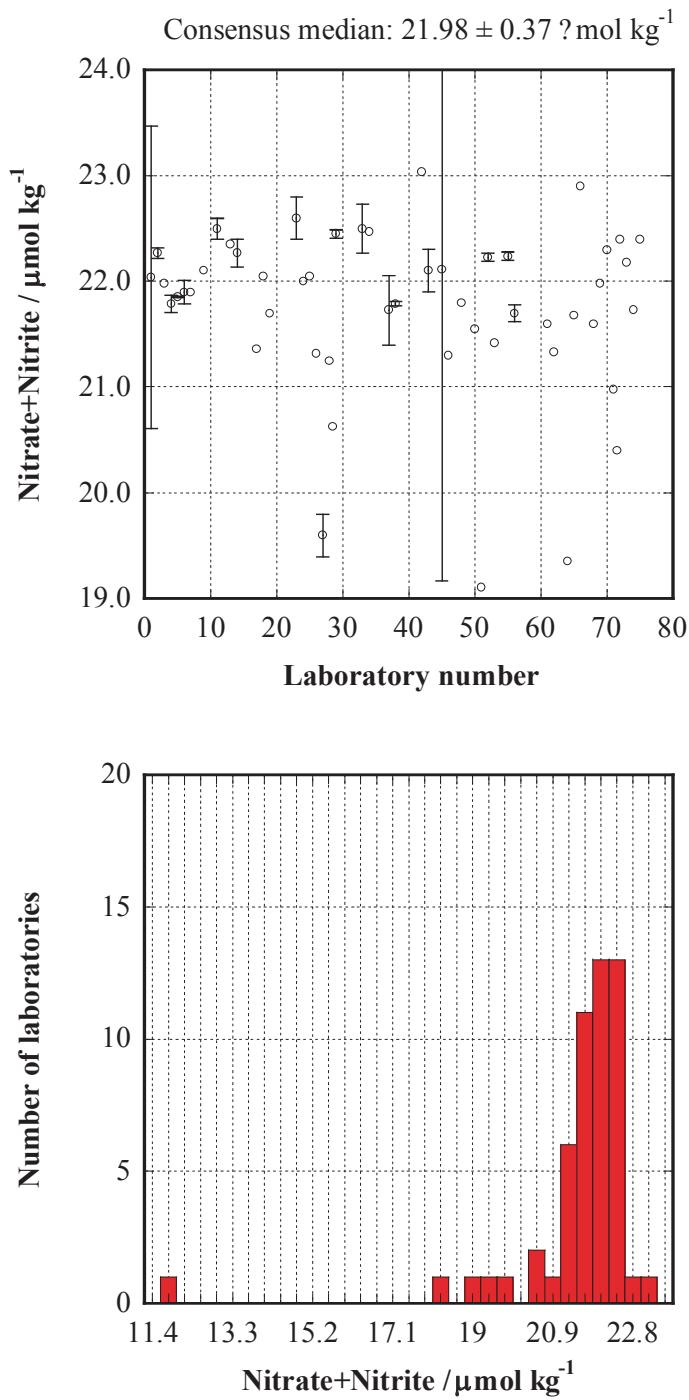
Lab #	Sample	Ammonia	Error	Nitrite	Error	Nitrate	Error	Nitrate+Nitrite	Error
7	2	2.93		0.033		29.9		29.9	
	3	1.97		0.016		41.34		41.36	
	4	1.1		0.022		0.06		0.08	
	8	4.91							
14	1	1.06	0.22	0.35	0	21.92		22.27	0.13
	2	1.84	0.04	0.02	0	29.92		29.94	0
	3	2.29	0.07	0.01	0	41.38		41.39	0.12
	4	1.01	0.08	0.01	0	0.06		0.07	0
	5	2.59	0.03	0.02	0	29.97		29.99	0.02
	6	0.82	0	0.61	0	5.84		6.43	0.01
17	1	2.4997		0.3623		21.0022		21.3645	
	2	4.0735		0.0482		29.3388		29.3869	
	3	4.1039		0.0274		40.6086		40.636	
	4	2.874		0.0397		0.5992		0.6389	
	5	3.2067		0.0429		29.5168		29.5597	
	6	2.15		0.6124		5.8249		6.4373	
19	8	4.73							
20	1	0.72		0.36				18.37	
	2	2.11		0.02					
	3	1.83		0					
	4	0.96		0.01				0.25	
	5	2.39		0.03					
	6	0.82		0.63				6.56	
	7	1.71		0.05					
	8	4.78		0				0.31	
27	1	1.38	0.2					19.6	0.2
	2	4.01	0.08					27.41	1.1
	3	2.22	0.07					38.42	0.5
	4	1.43	0.04					0.15	0.05
	5	2.72	0.22					25.95	0.6
	6	1.16	0.08					4.78	0.2
28-1	1	0.75		0.36		20.89		21.25	
	2	2.7		0.05		21.54		21.59	
	3	2.21		0.04		57.55		57.58	
	4	1.22		0.04		0.07		0.11	
	5	2.48		0.05		29.18		29.24	
	6	0.88		0.63		5.46		6.1	

## **Appendix III**

**Scatter plots and histograms of the results from participating laboratories**

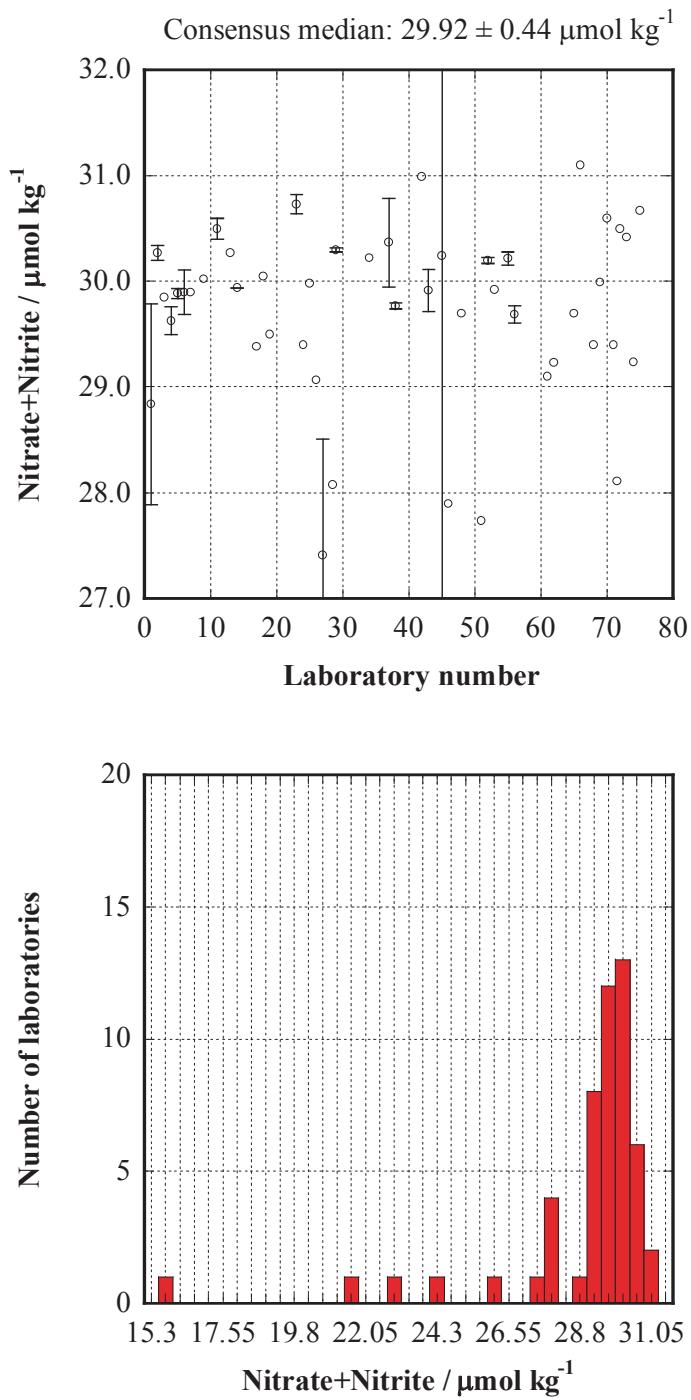


## Sample 1 Nitrate+Nitrite



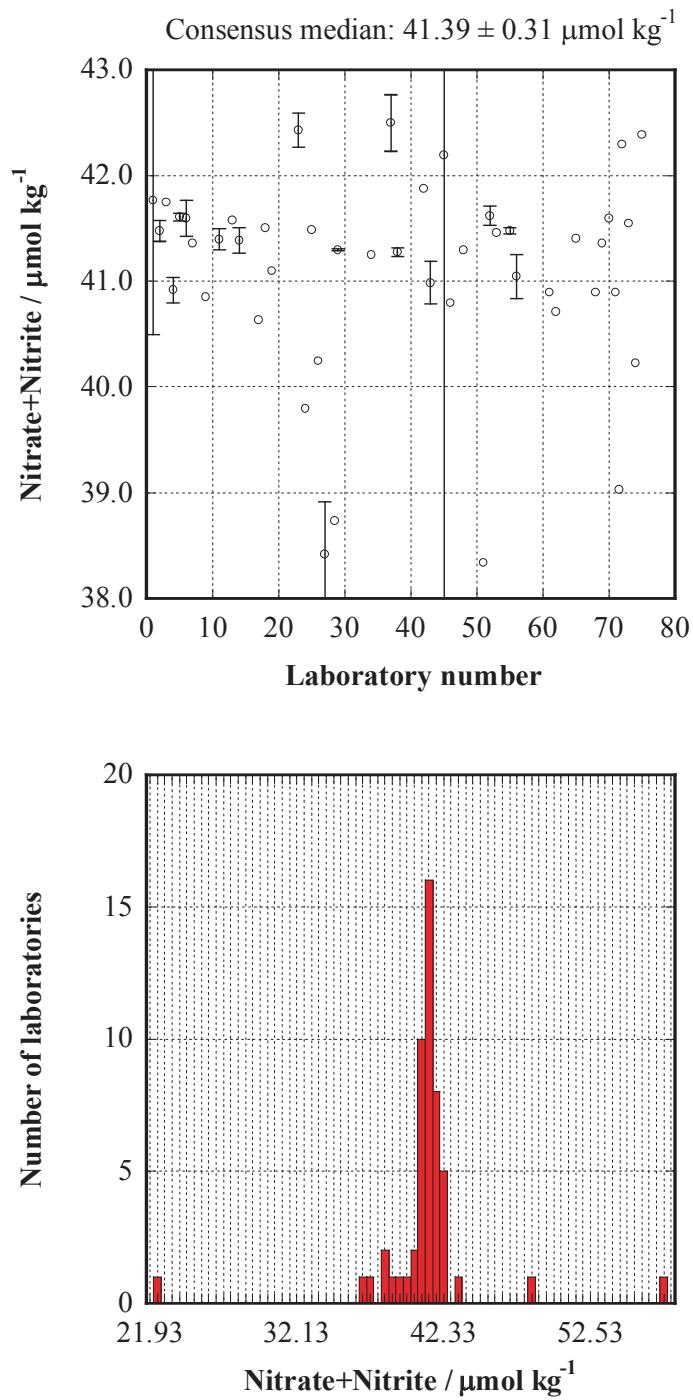
**Figure A1-1 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #1 (lower panel)**

## Sample 2 Nitrate+Nitrite



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

## Sample 3 Nitrate+Nitrite



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

## Sample 4 Nitrate+Nitrite

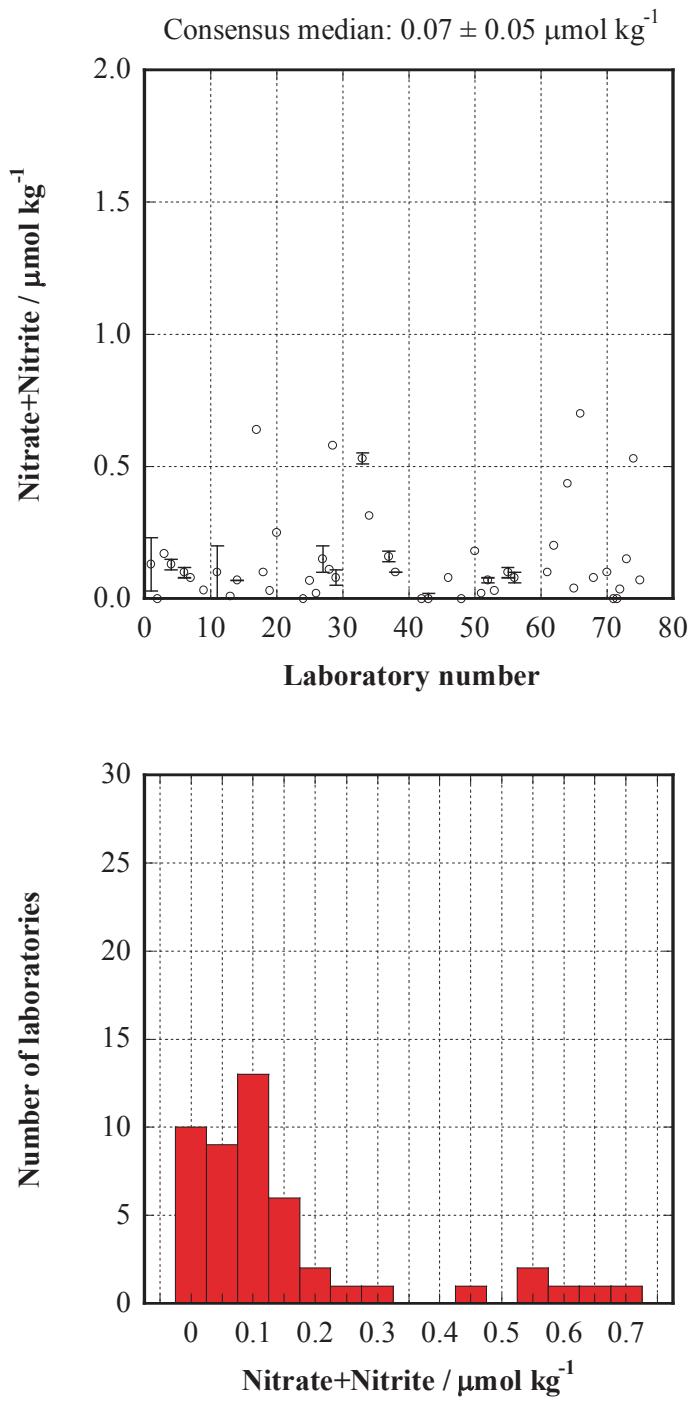
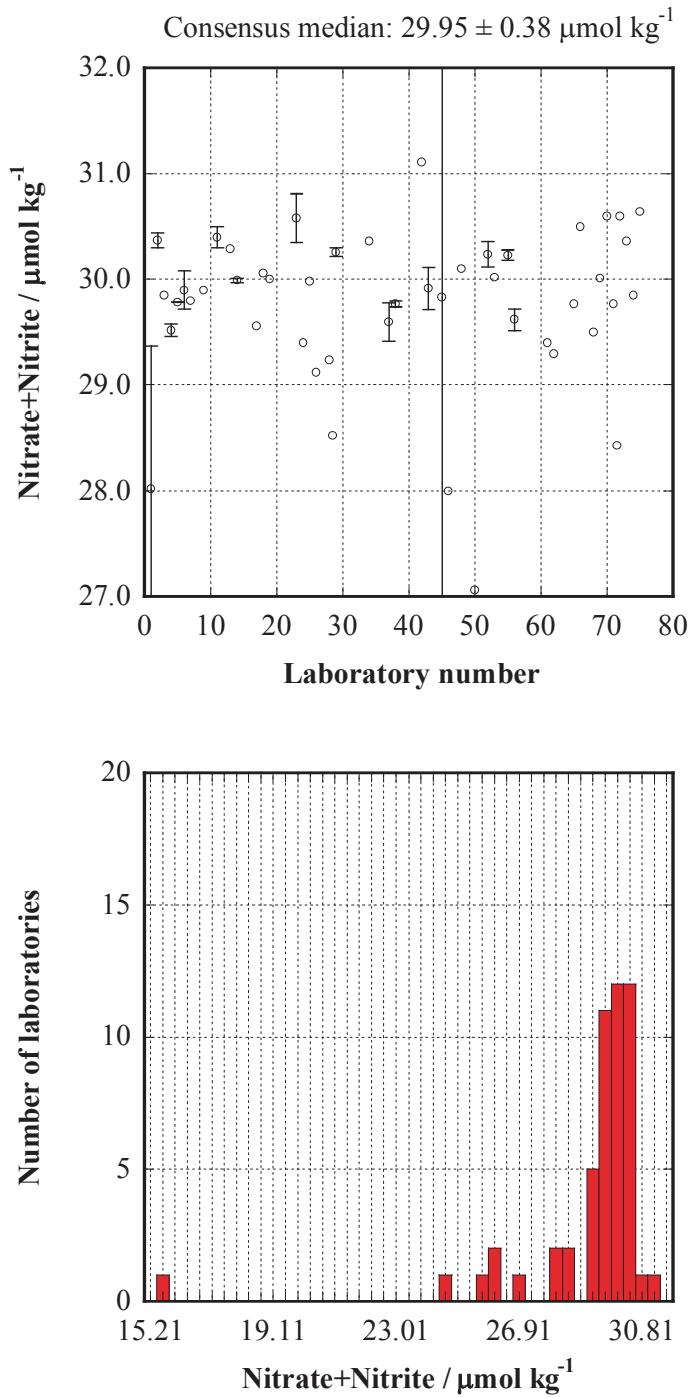


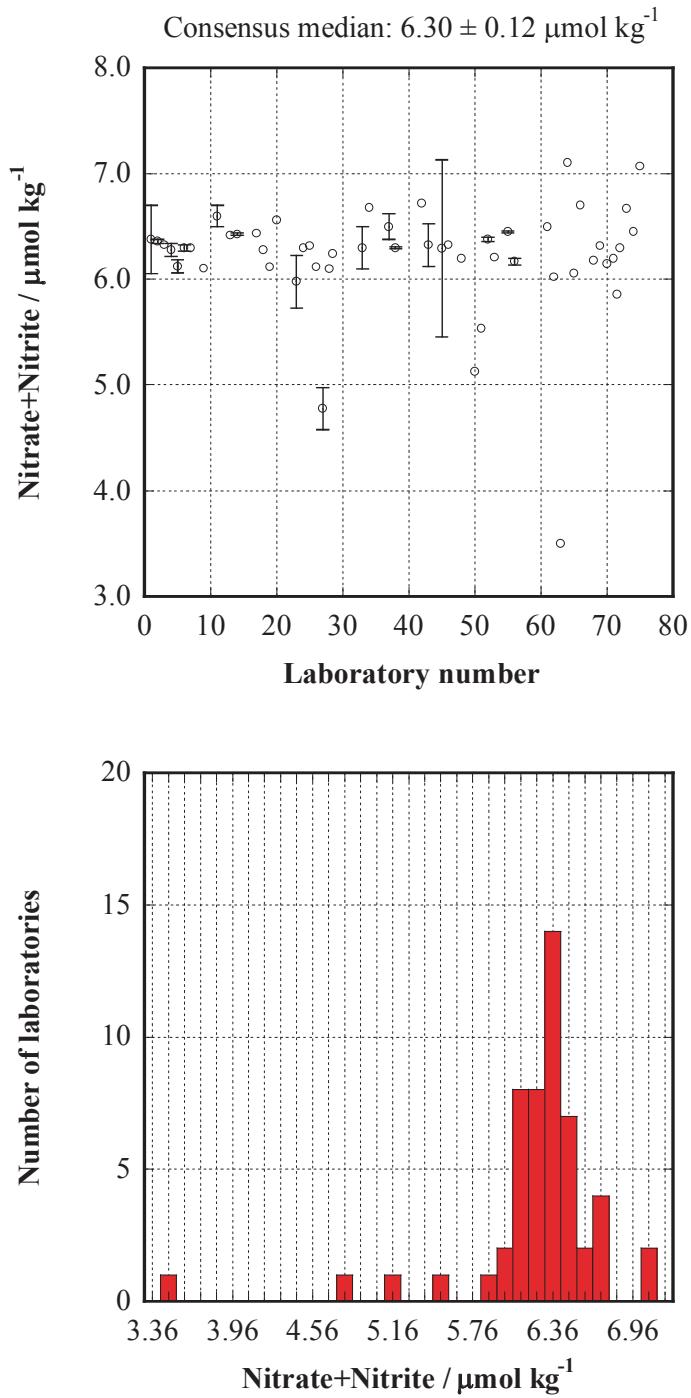
Figure A1-4 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #4 (lower panel)

## Sample 5 Nitrate+Nitrite



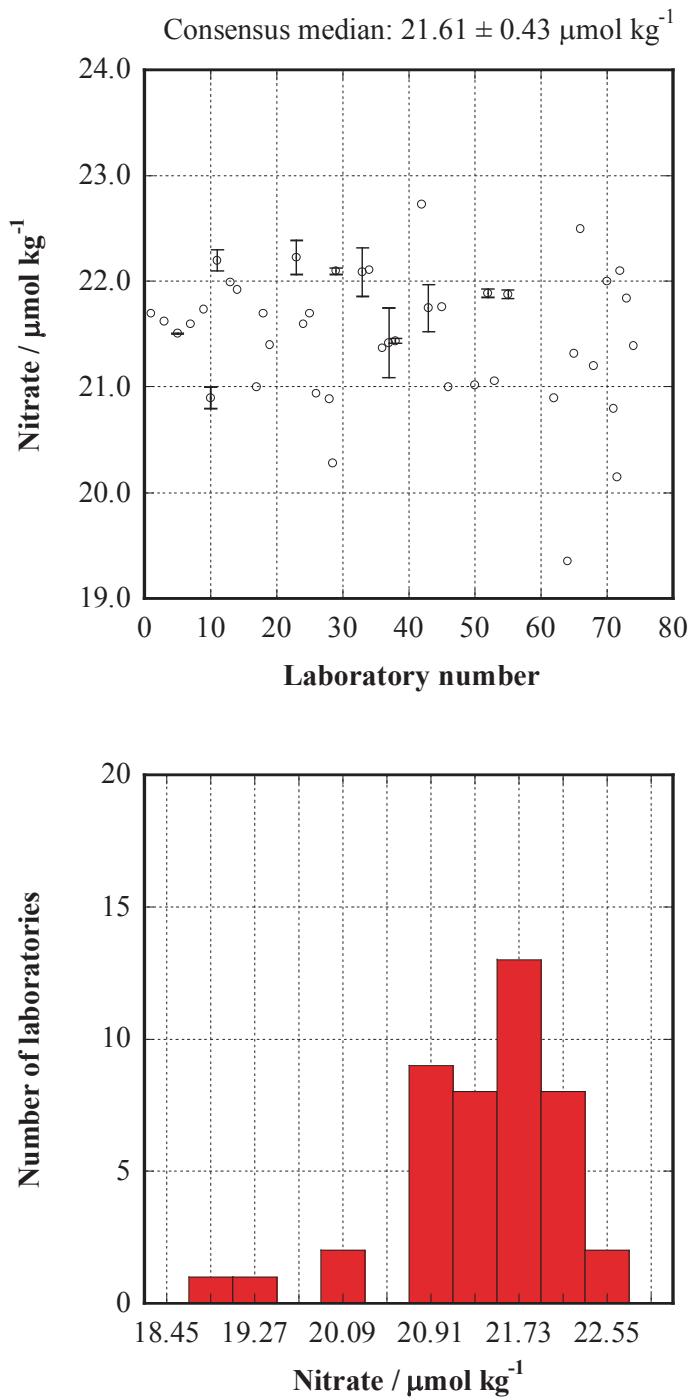
**Figure A1-5 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #5 (lower panel)**

## Sample 6 Nitrate+Nitrite



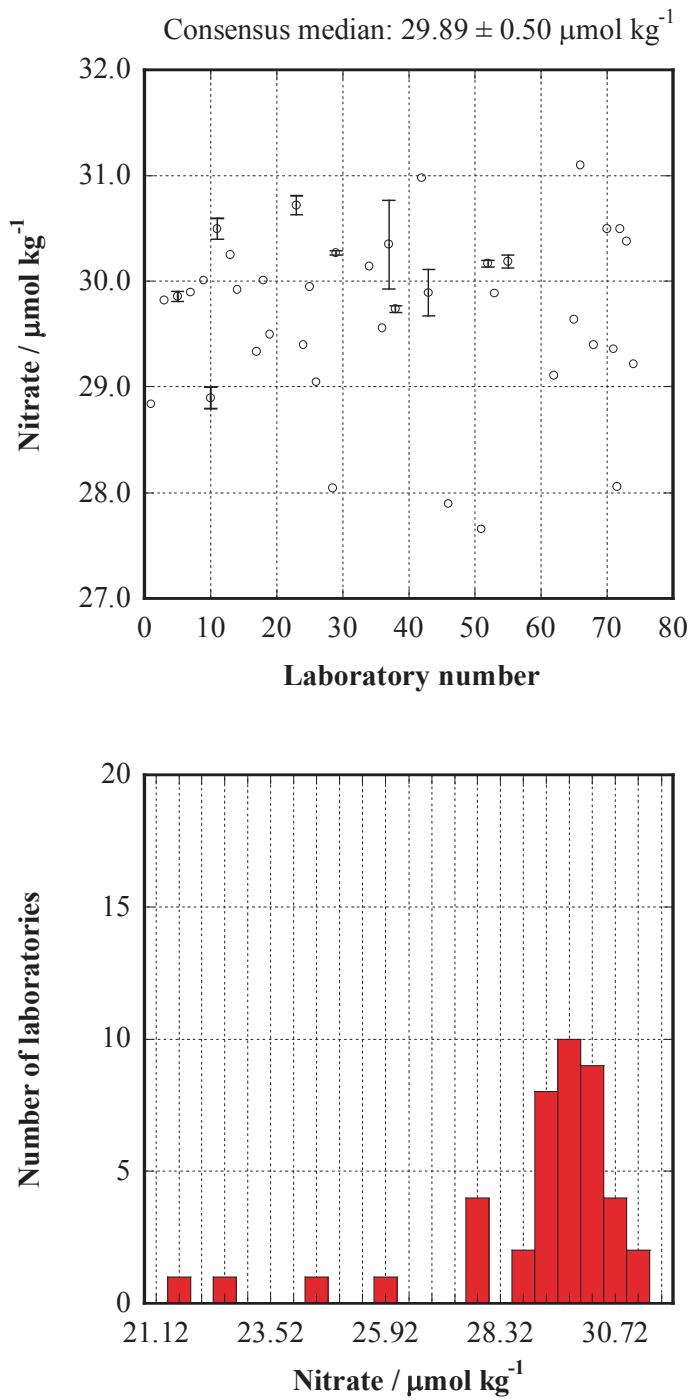
**Figure A1-6 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #6 (lower panel)**

## Sample 1 Nitrate



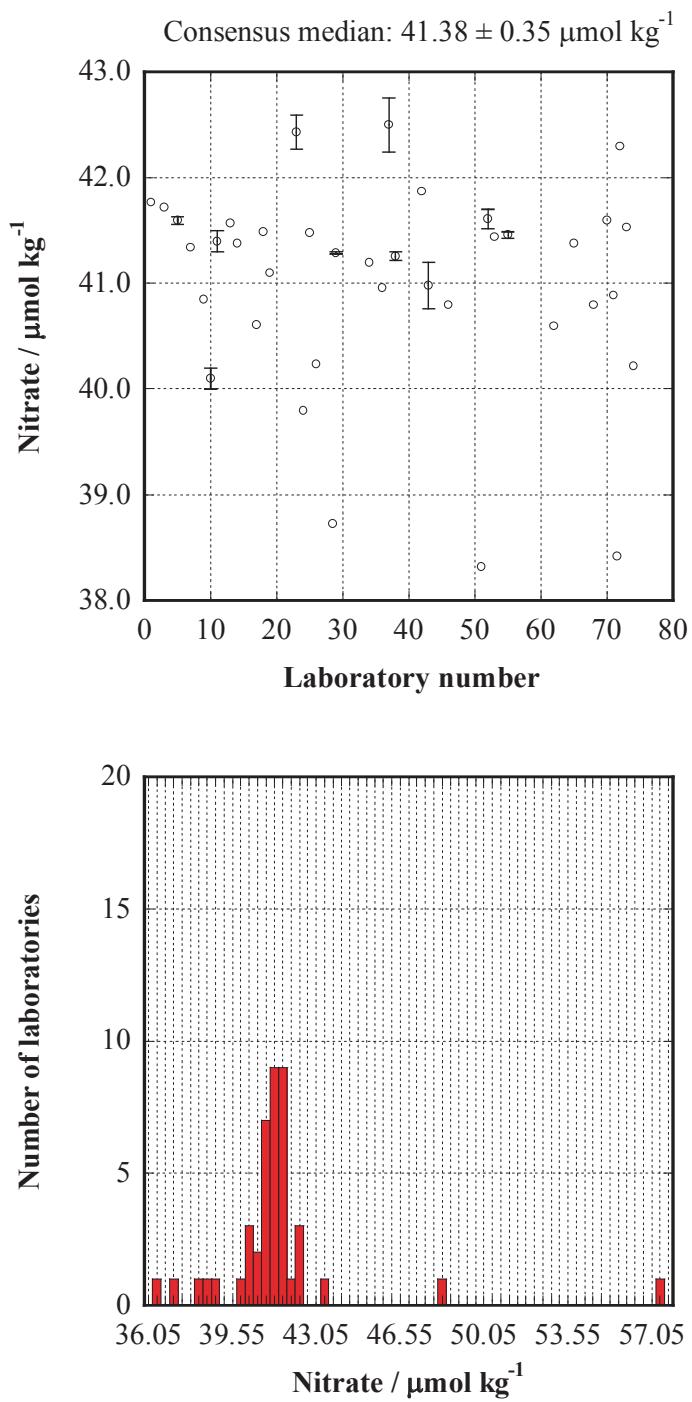
**Figure A2-1 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #1 (lower panel)**

## Sample 2 Nitrate



**Figure A2-2 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #2 (lower panel)**

## Sample 3 Nitrate



**Figure A2-3 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #3 (lower panel)**

## Sample 4 Nitrate

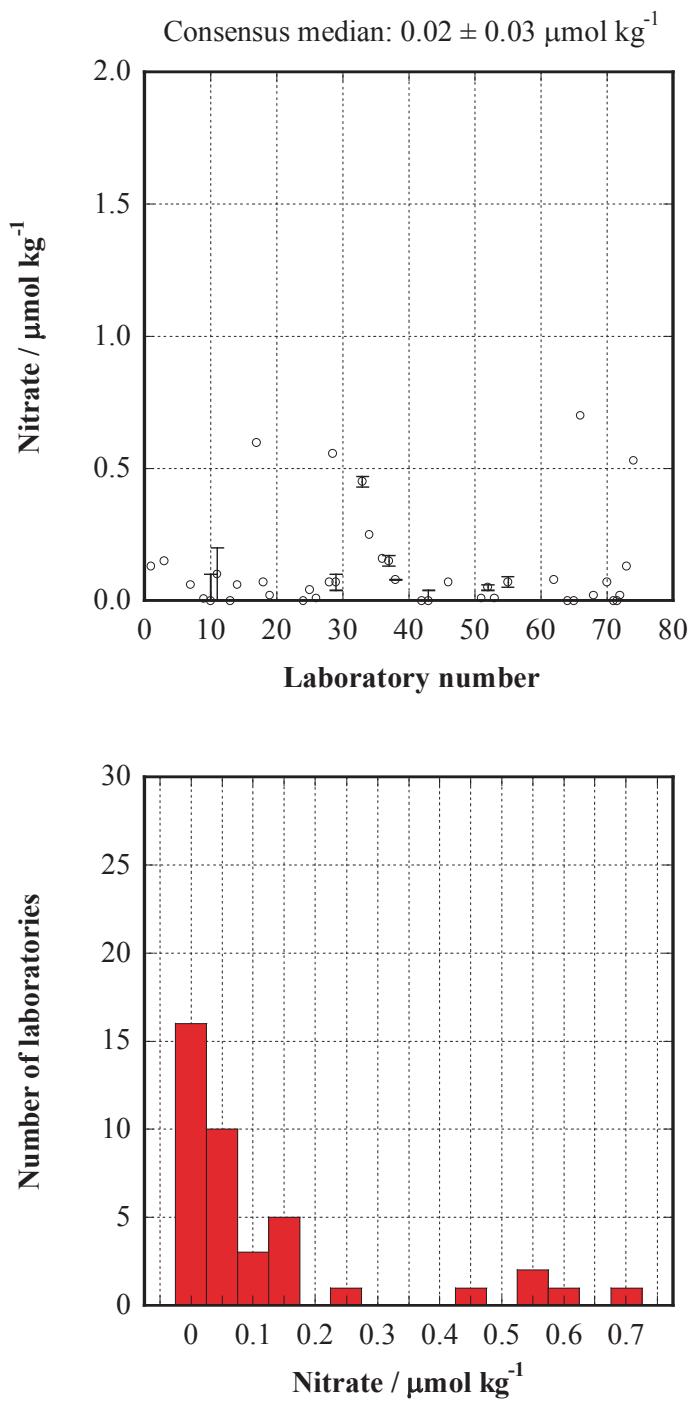


Figure A2-4 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #4 (lower panel)

## Sample 5 Nitrate

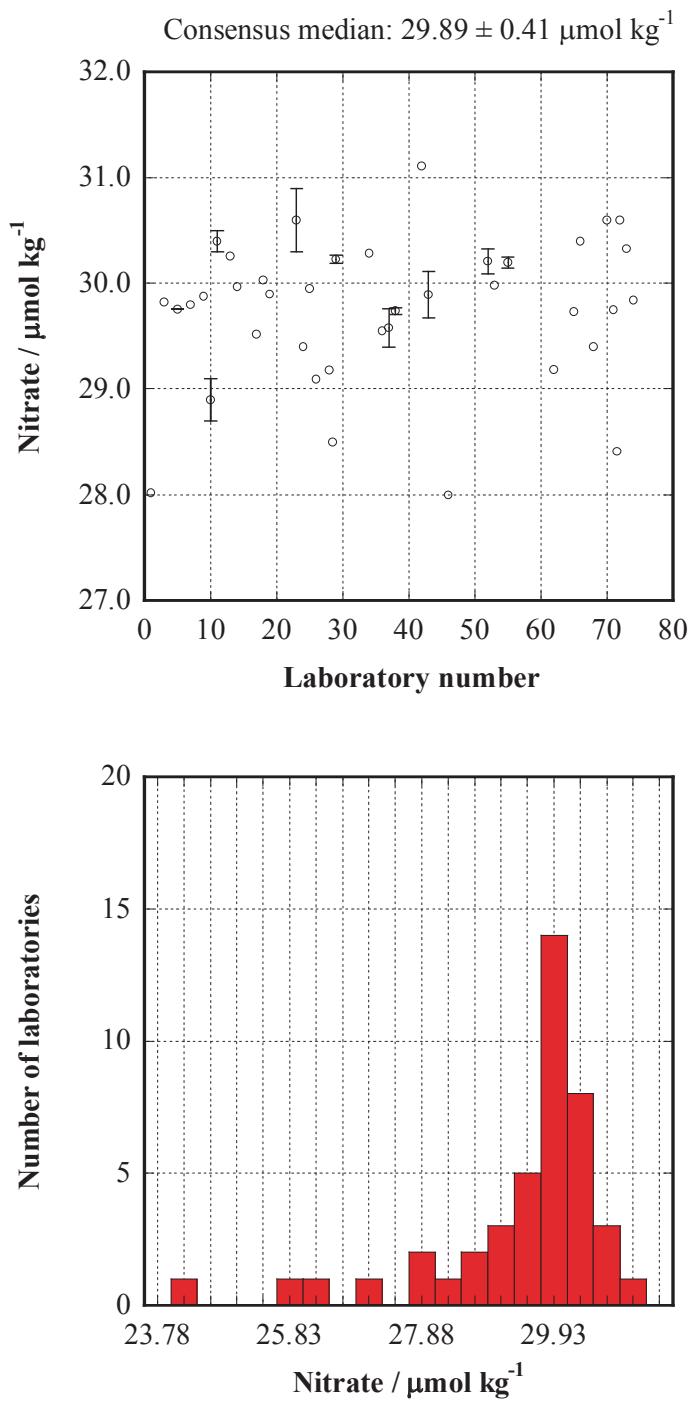


Figure A2-5 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #5 (lower panel)

## Sample 6 Nitrate

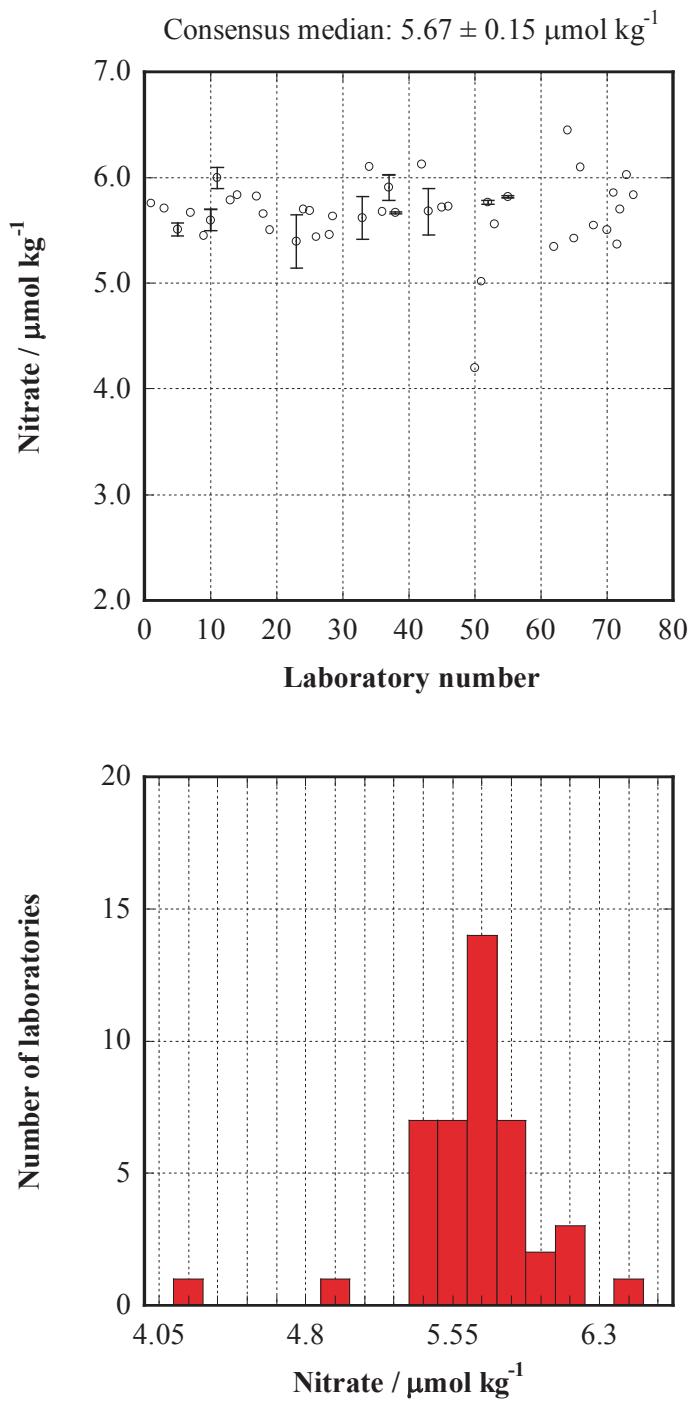


Figure A2-6 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #6 (lower panel)

## Sample 1 Nitrite

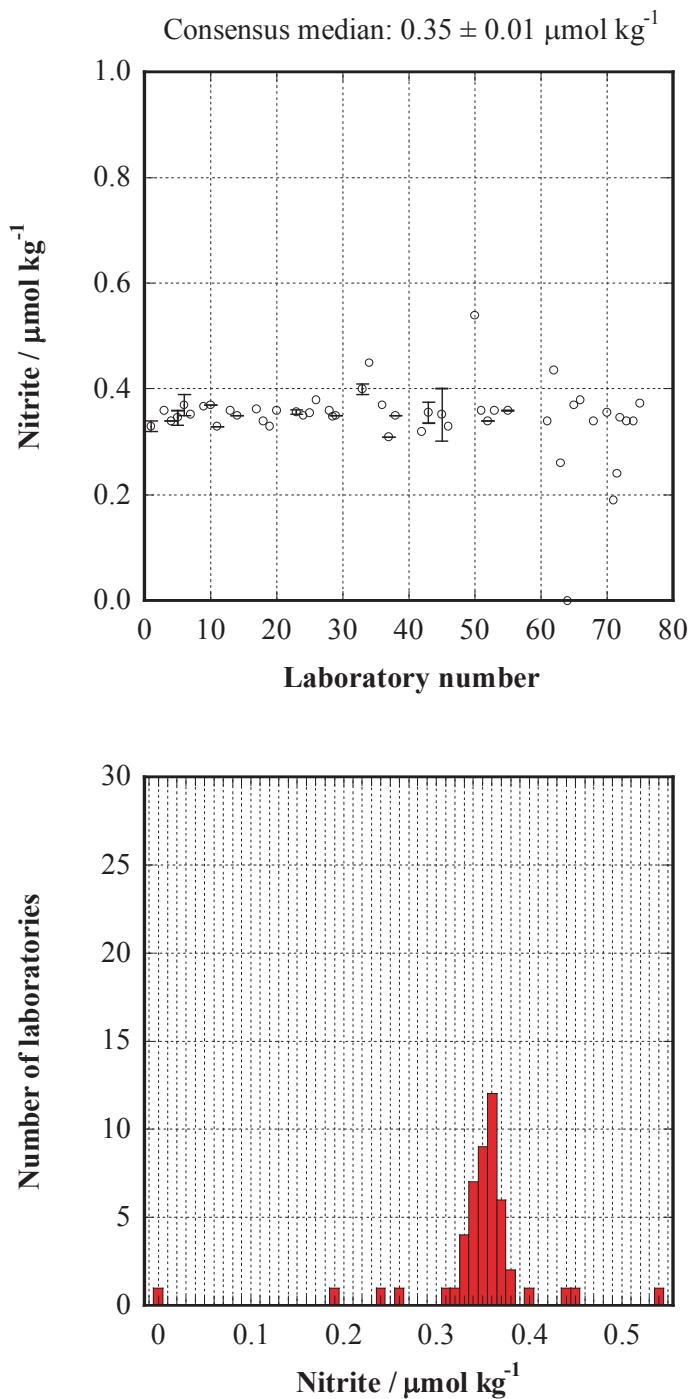


Figure A3-1 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #1 (lower panel)

## Sample 2 Nitrite

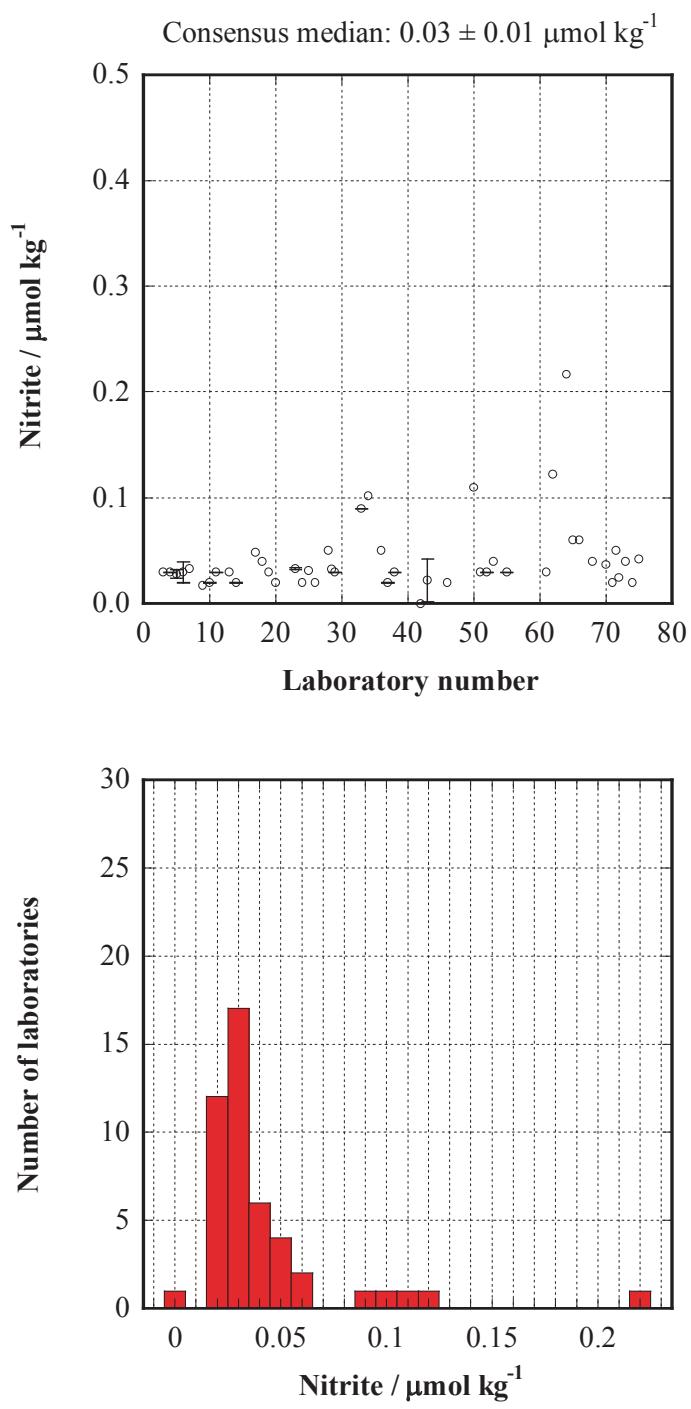


Figure A3-2 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #2 (lower panel)

## Sample 3 Nitrite

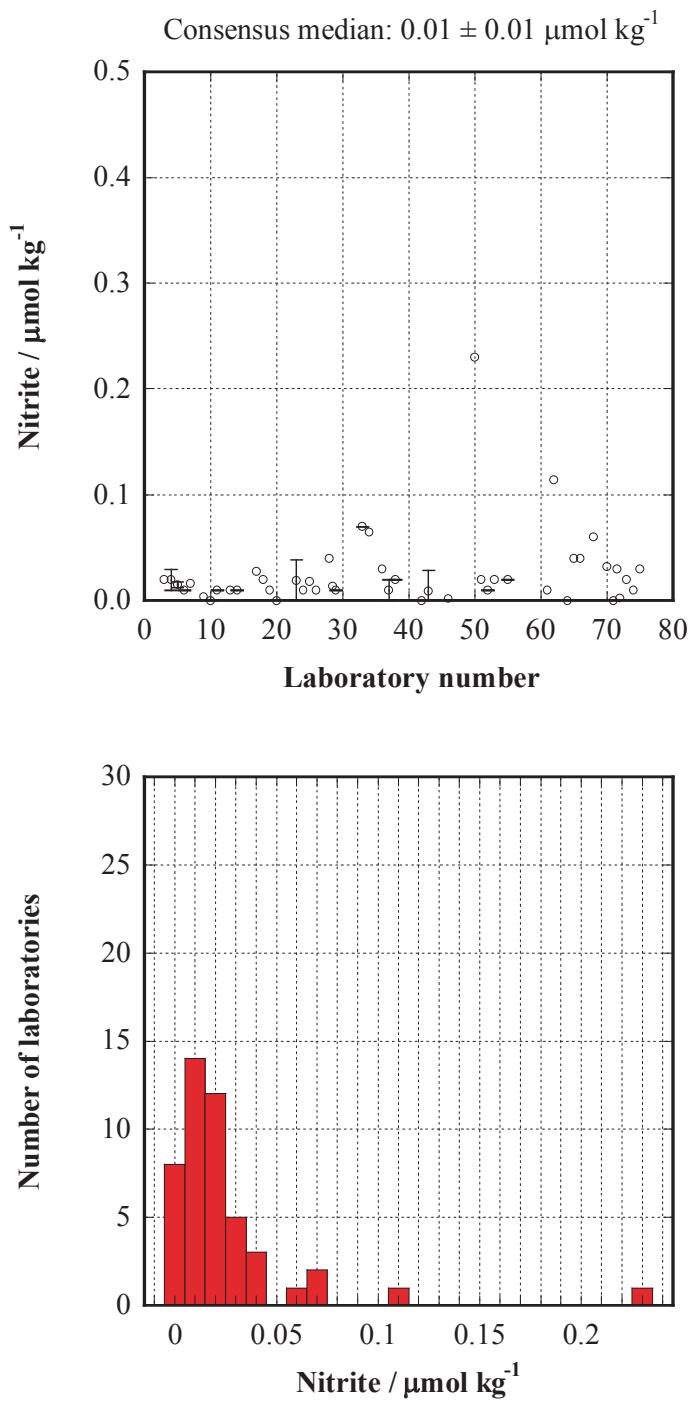


Figure A3-3 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #3 (lower panel)

## Sample 4 Nitrite

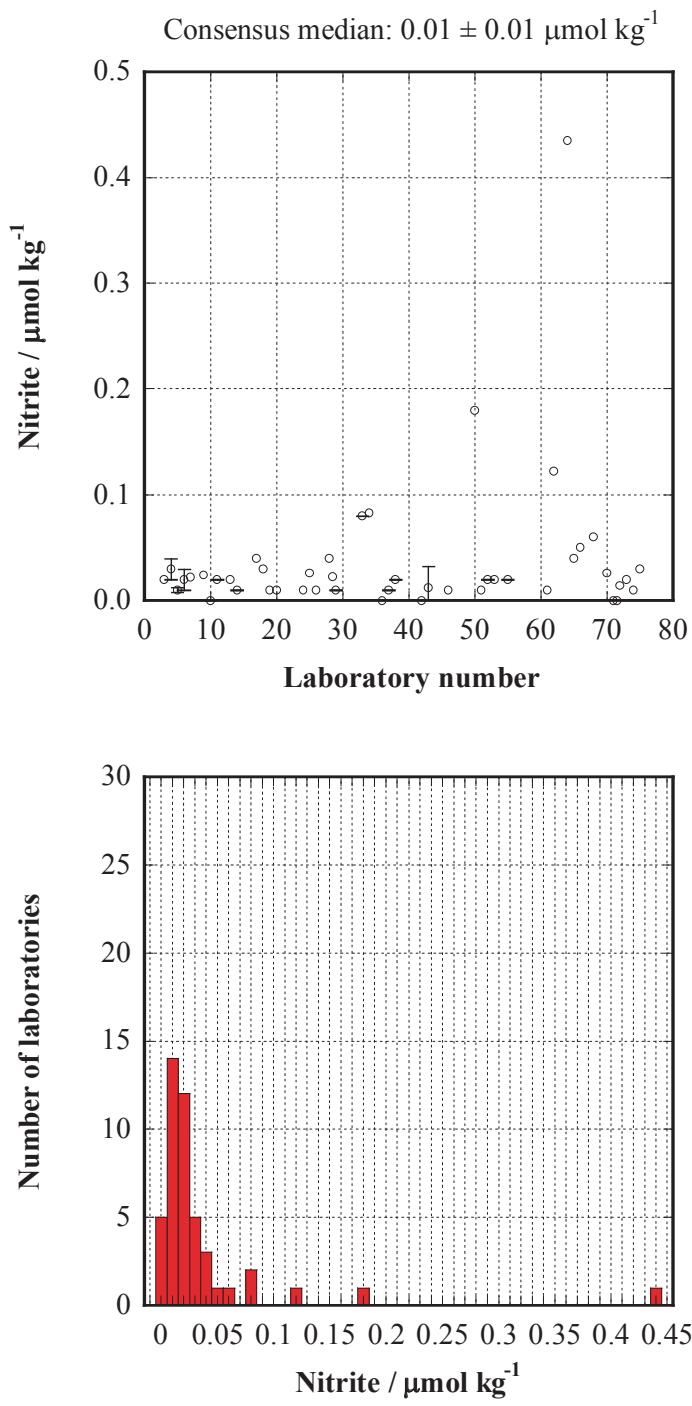


Figure A3-4 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #4 (lower panel)

## Sample 5 Nitrite

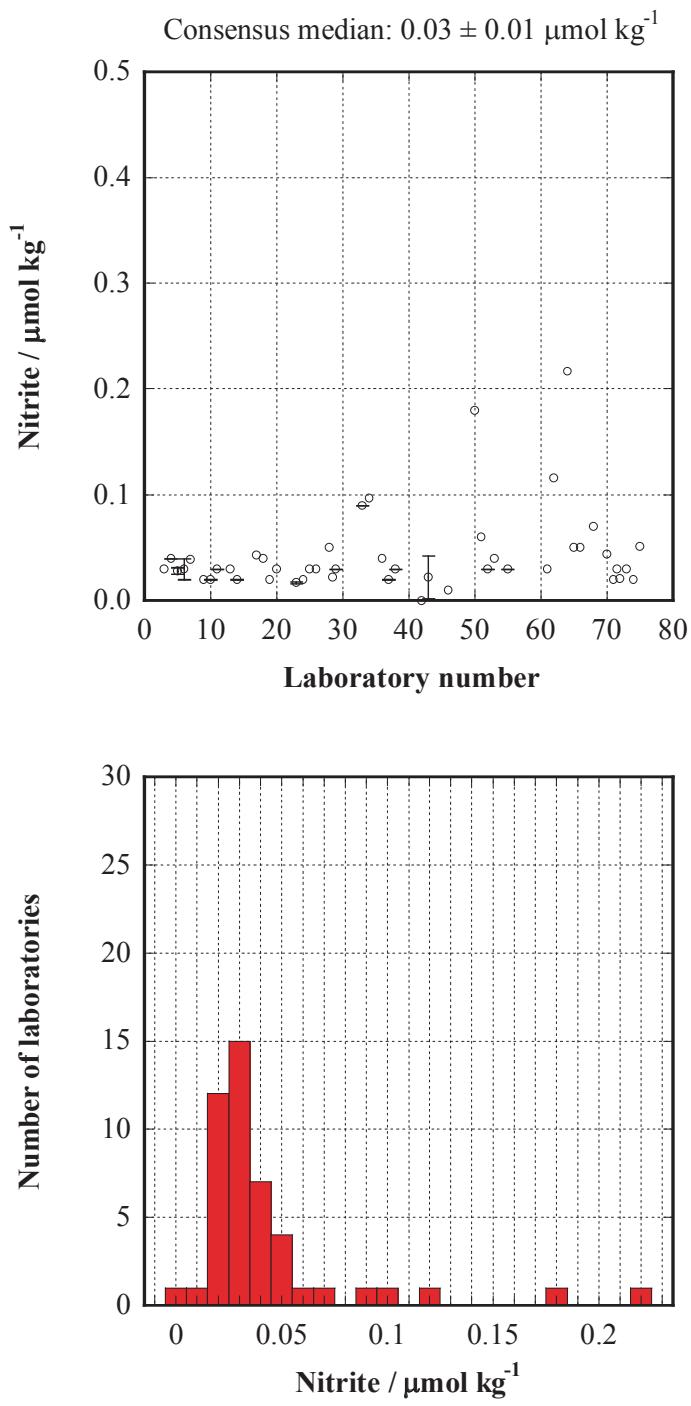


Figure A3-5 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #5 (lower panel)

## Sample 6 Nitrite

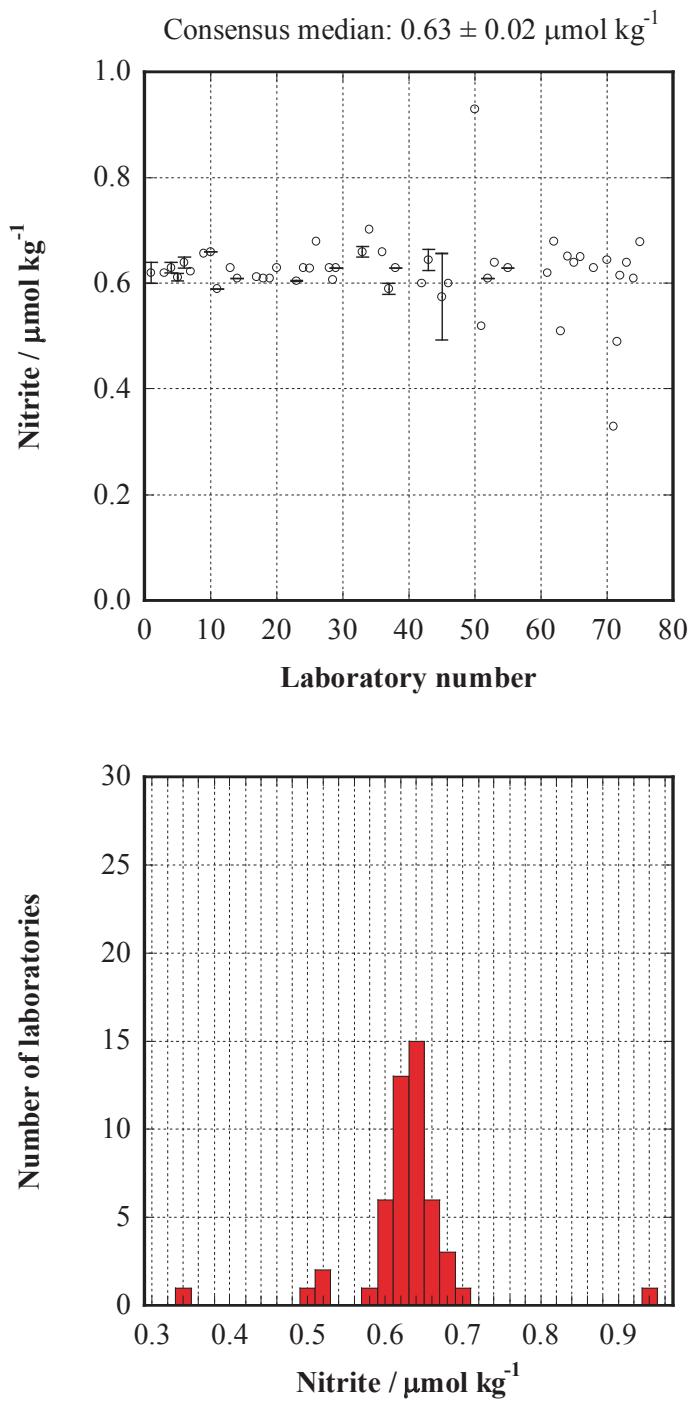
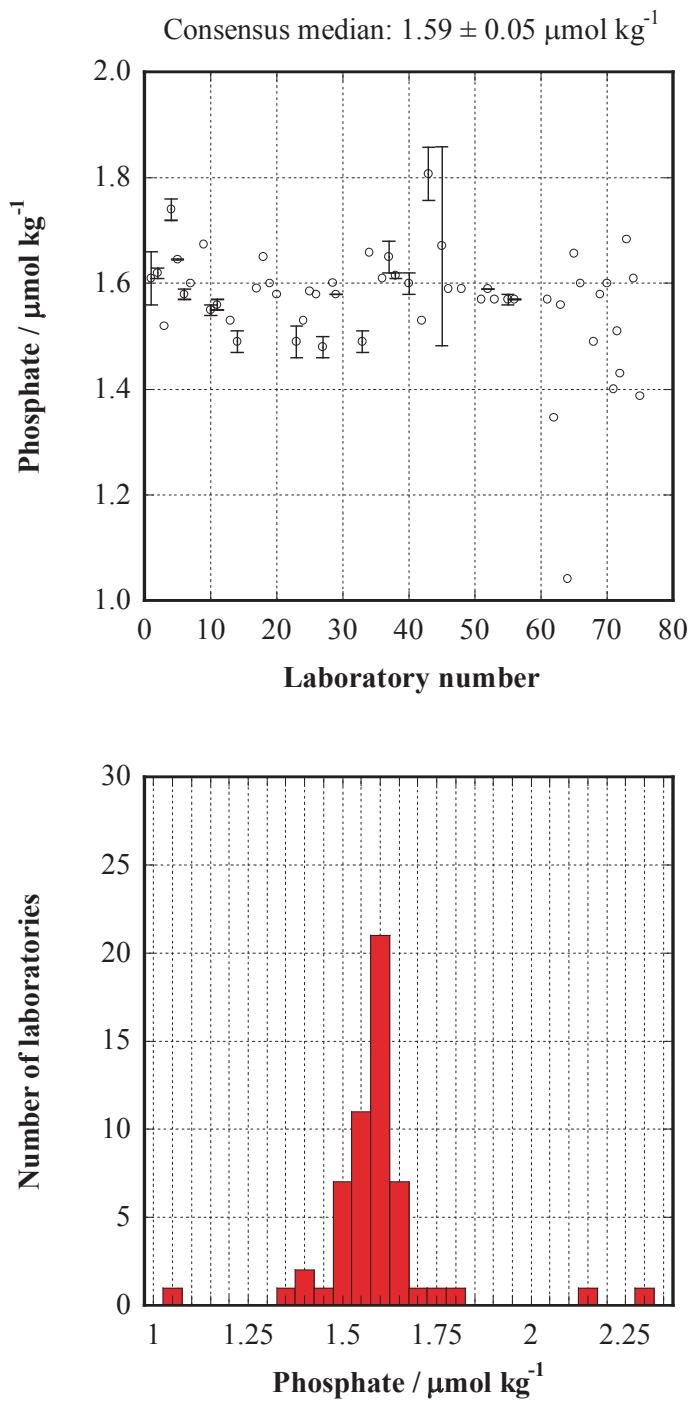


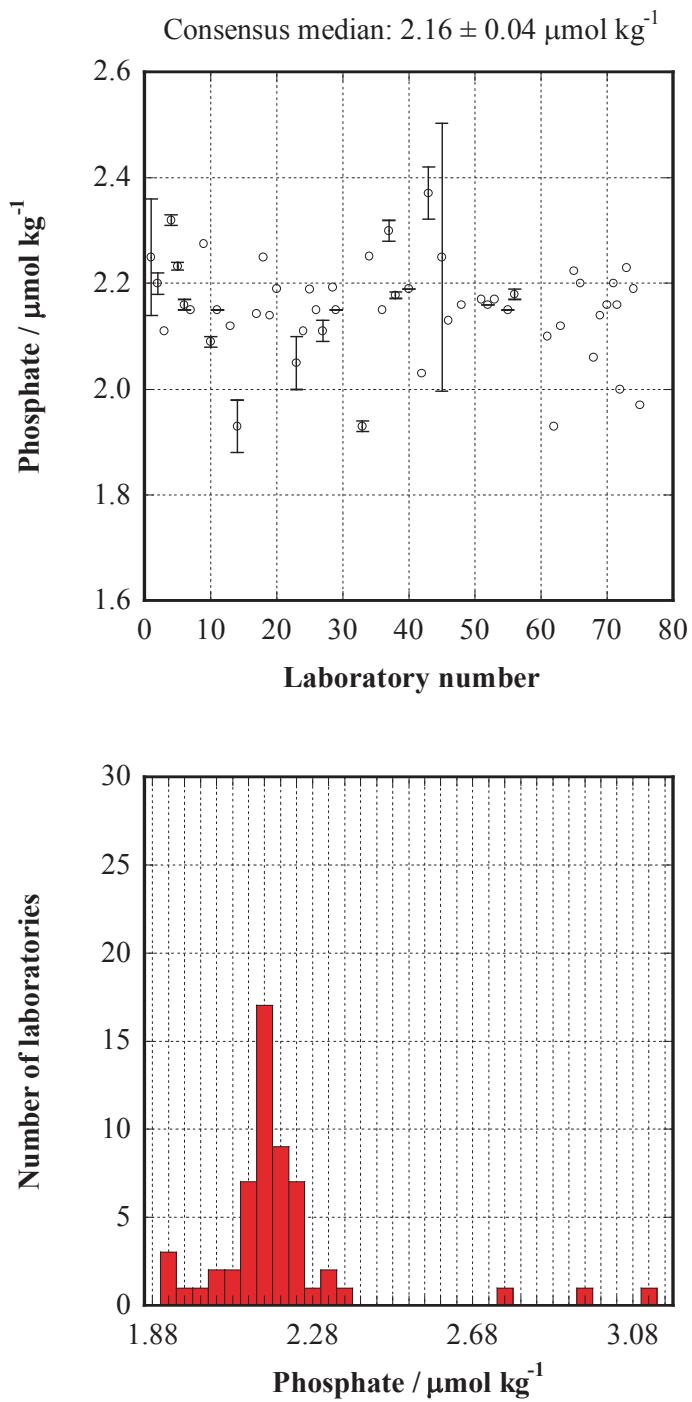
Figure A3-6 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #6 (lower panel)

## Sample 1 Phosphate



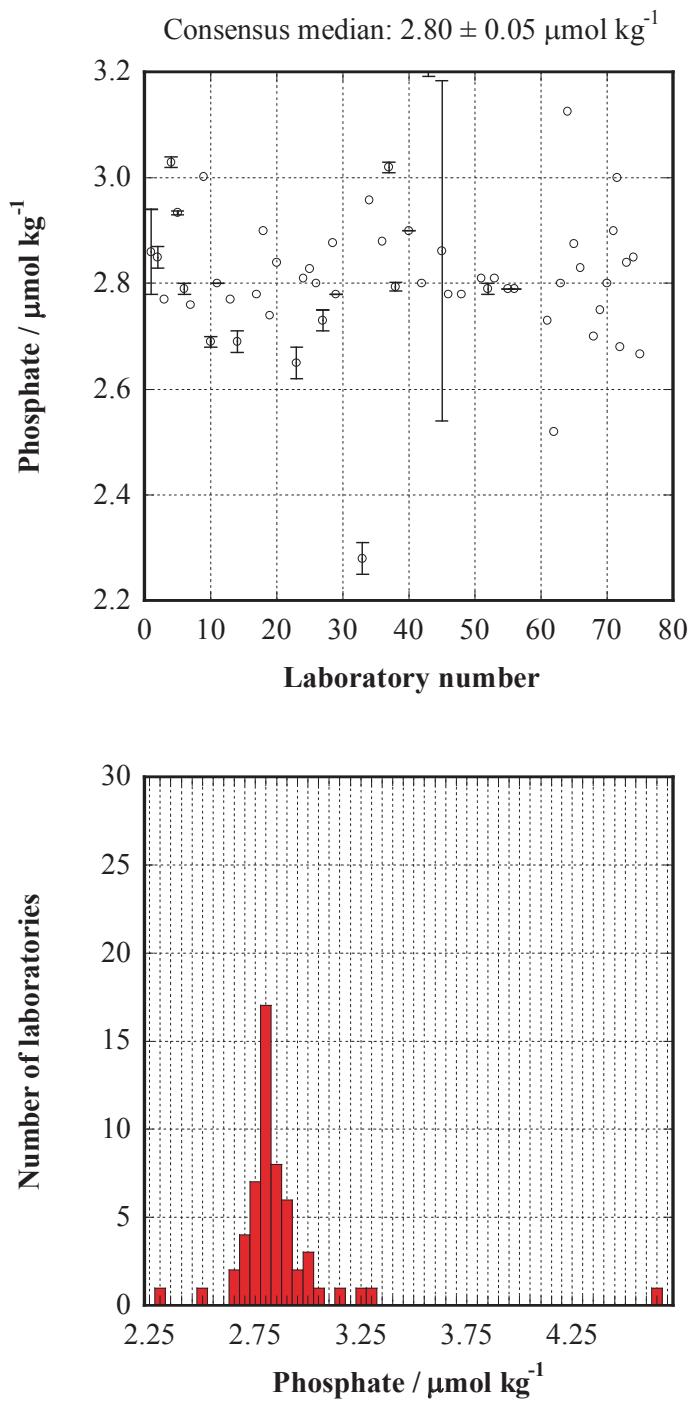
**Figure A4-1 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #1 (lower panel)**

## Sample 2 Phosphate



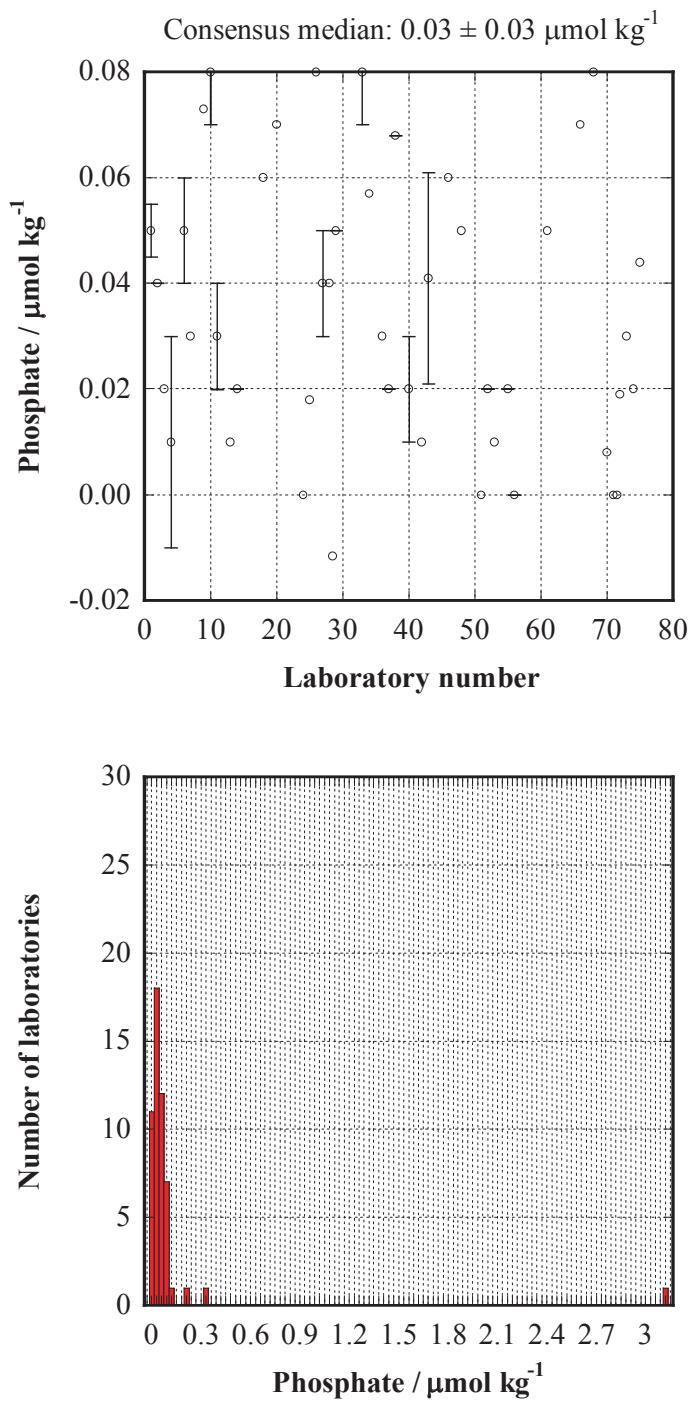
**Figure A4-2 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #2 (lower panel)**

## Sample 3 Phosphate



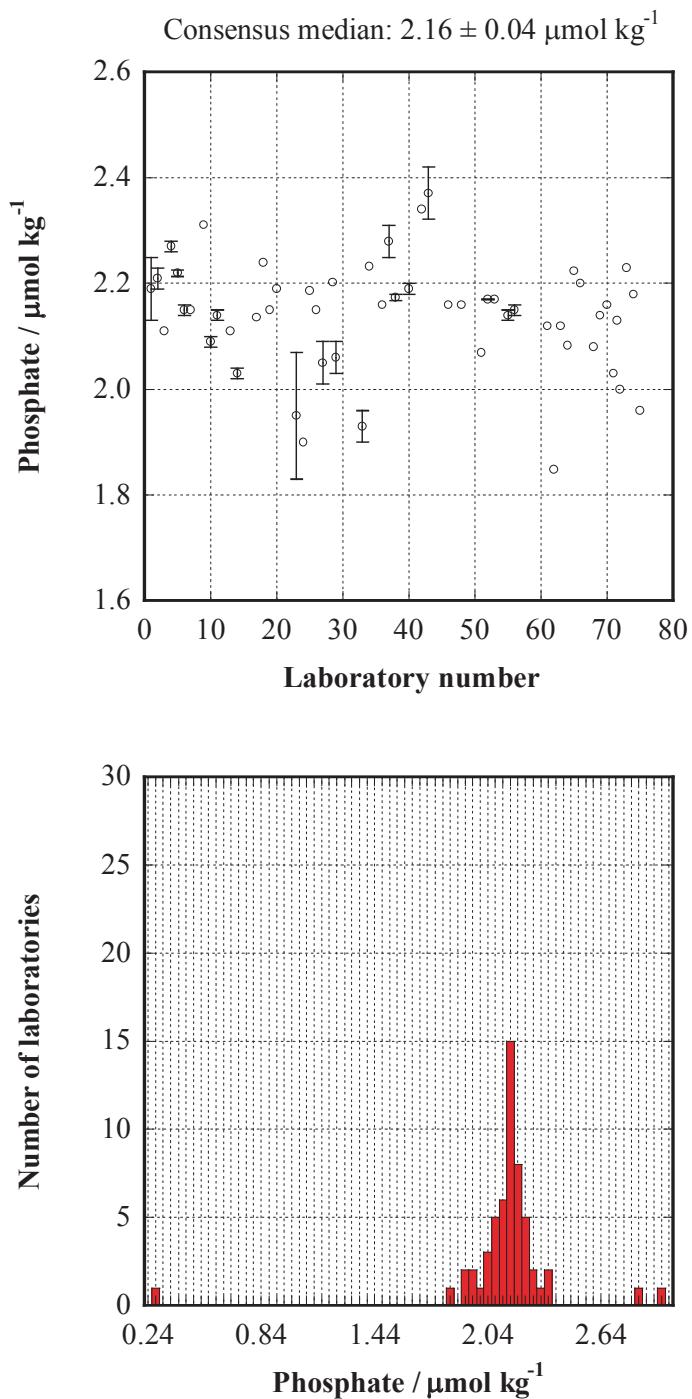
**Figure A4-3 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #3 (lower panel)**

## Sample 4 Phosphate



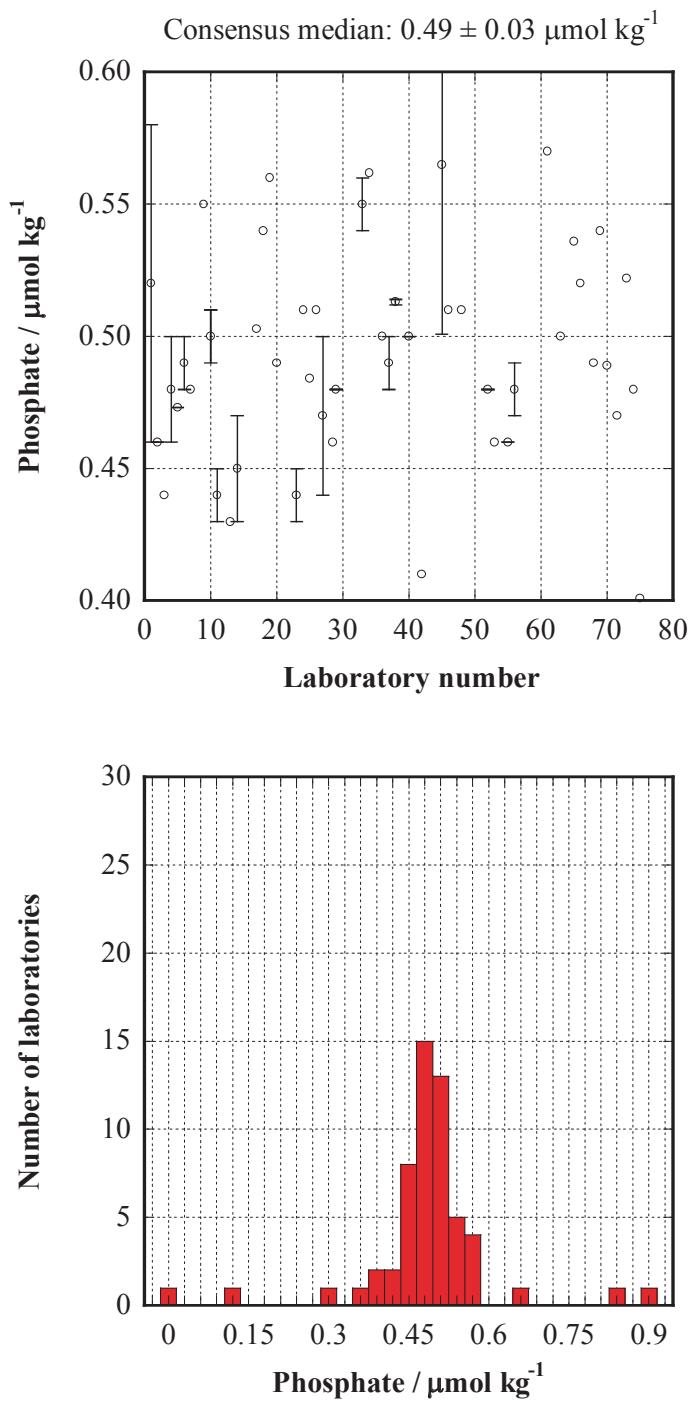
**Figure A4-4 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #4 (lower panel)**

## Sample 5 Phosphate



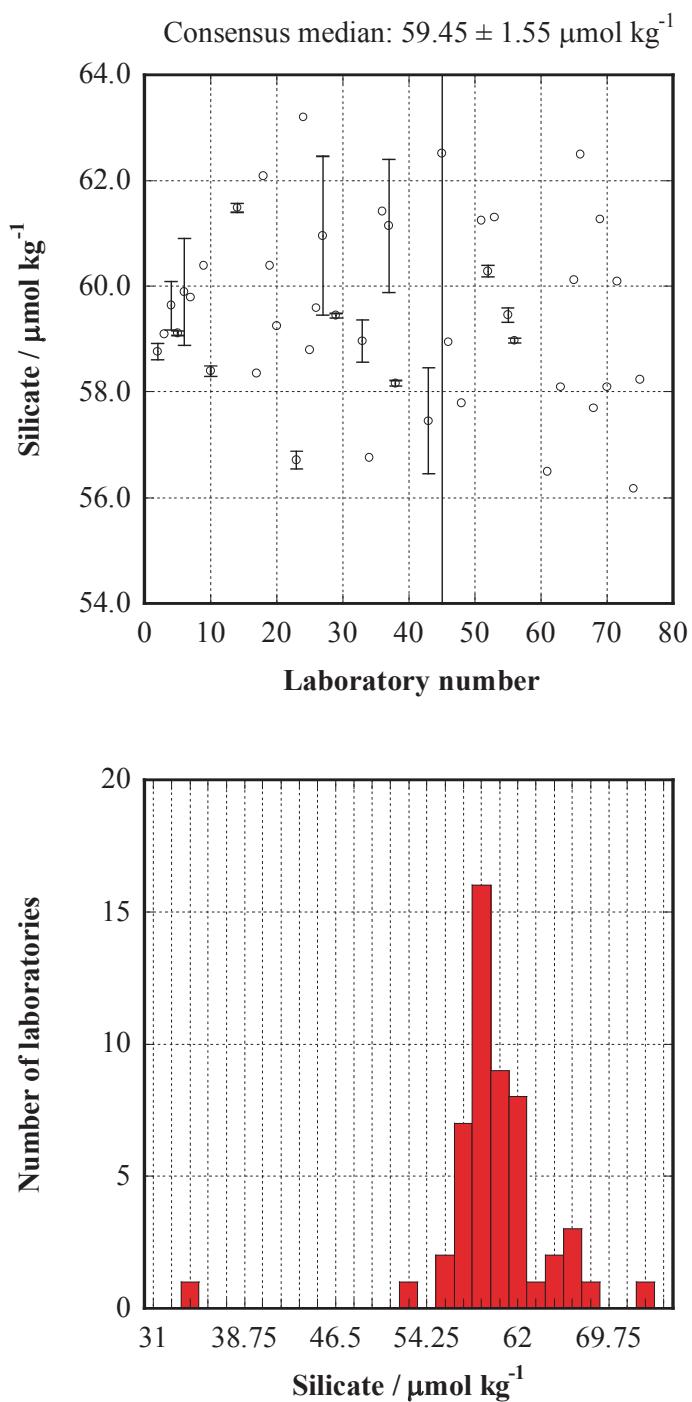
**Figure A4-5 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #5 (lower panel)**

## Sample 6 Phosphate



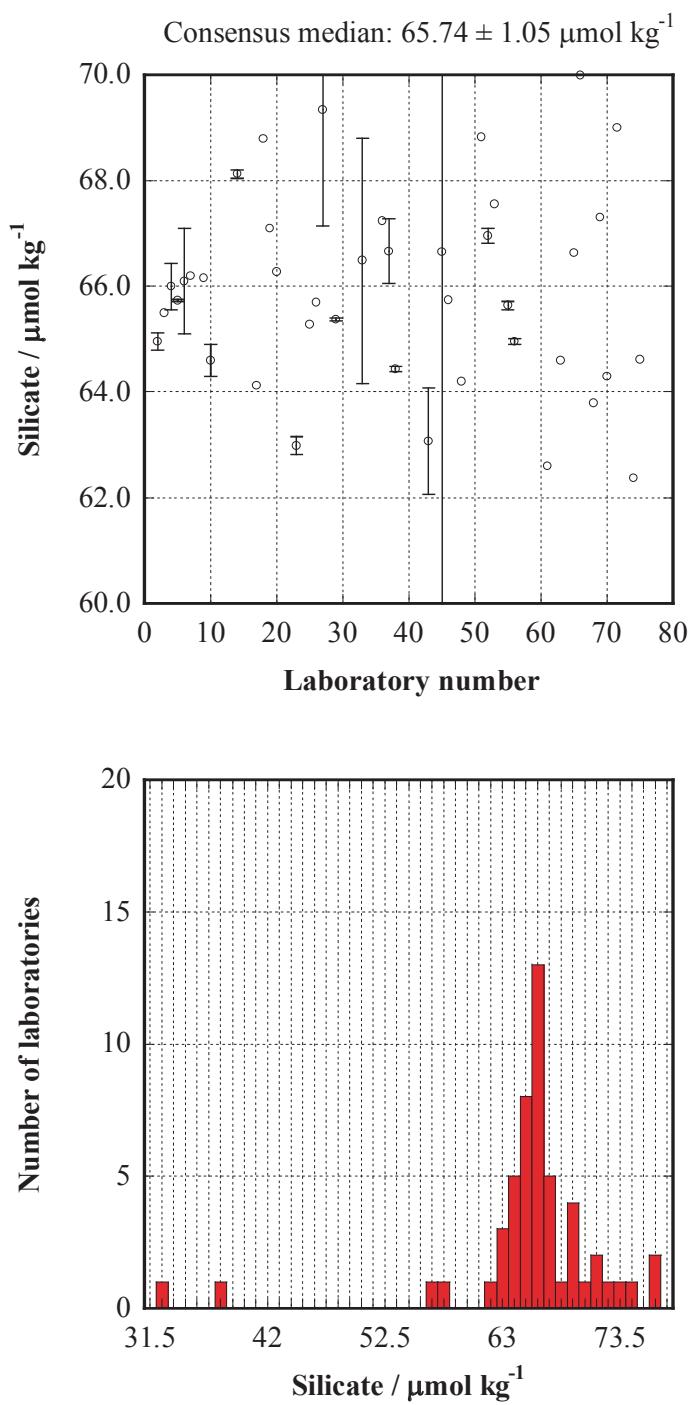
**Figure A4-6 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #6 (lower panel)**

## Sample 1 Silicate



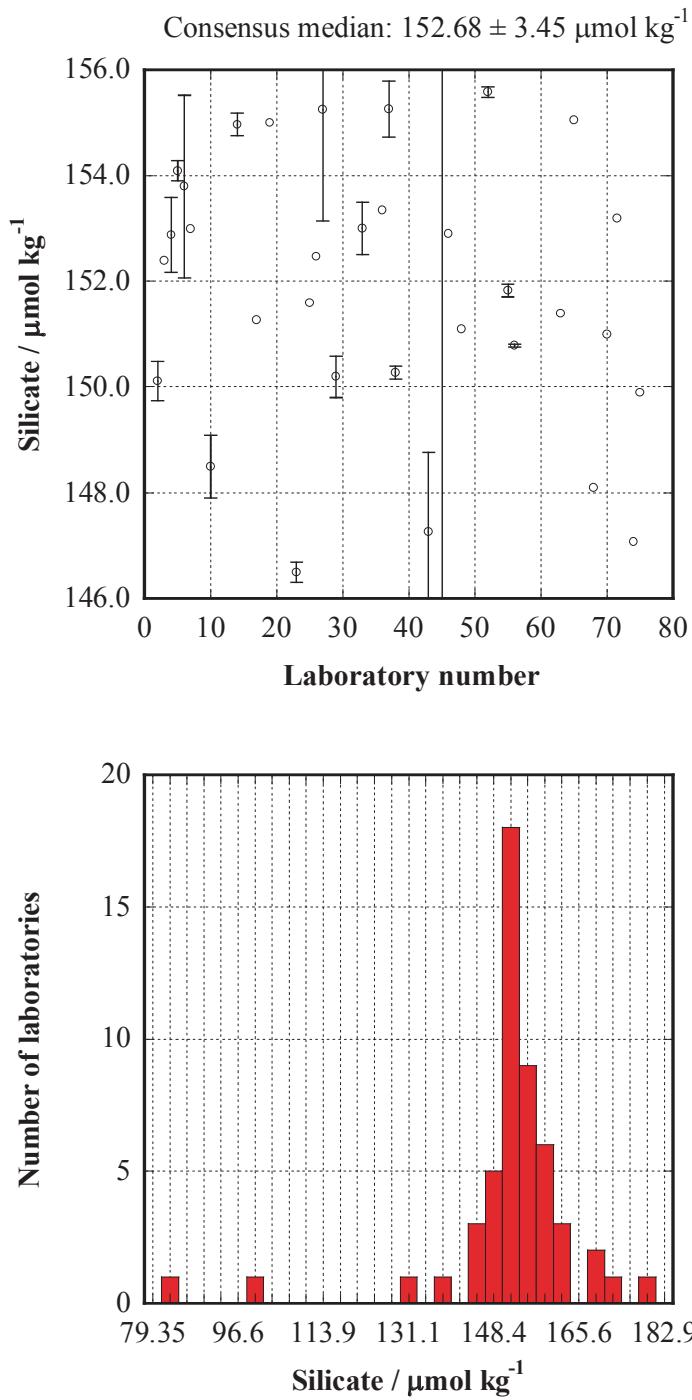
**Figure A5-1 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #1 (lower panel)**

## Sample 2 Silicate



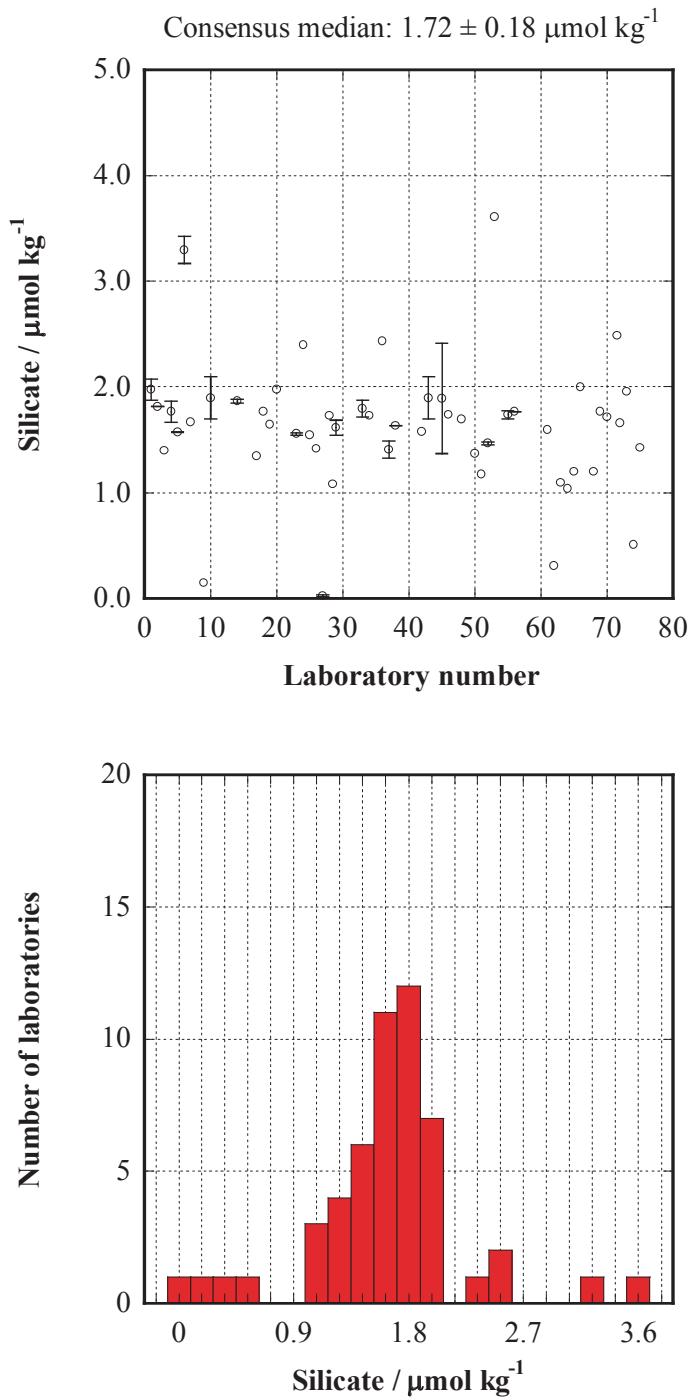
**Figure A5-2 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #2 (lower panel)**

## Sample 3 Silicate



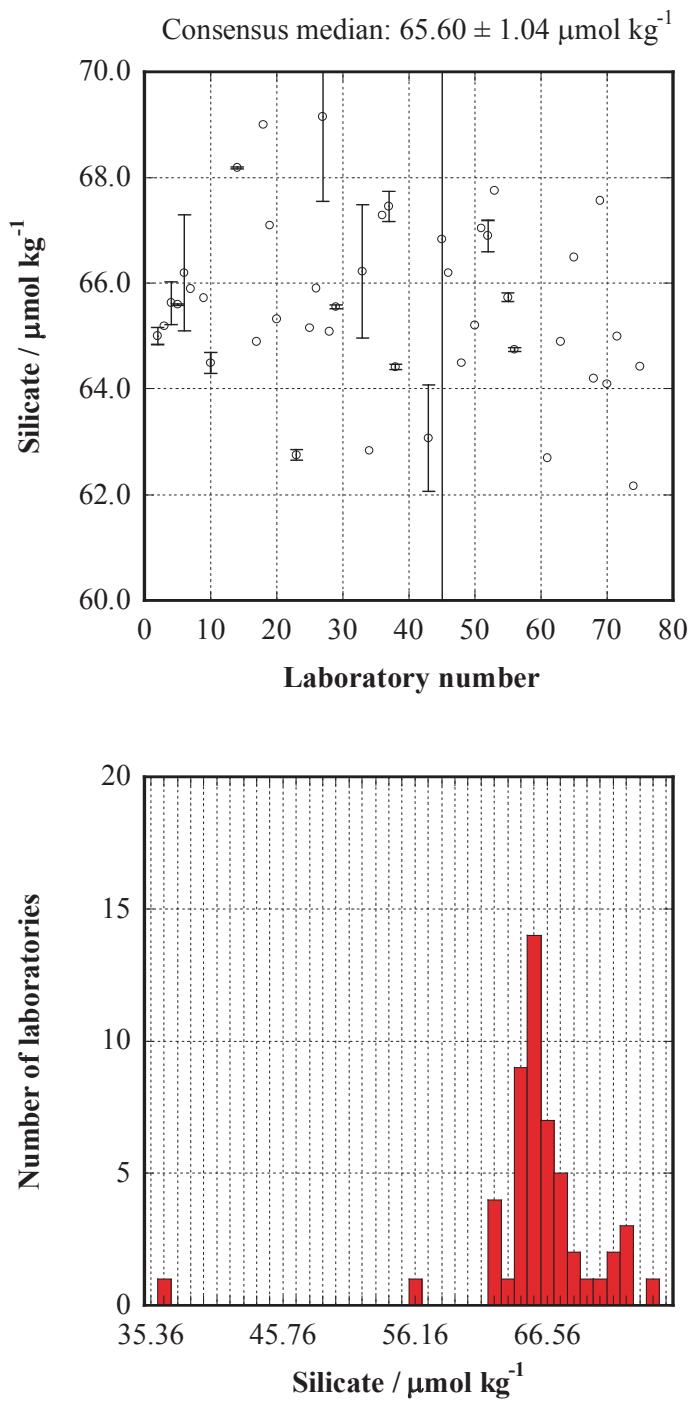
**Figure A5-3 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration of sample #3 (lower panel)**

## Sample 4 Silicate



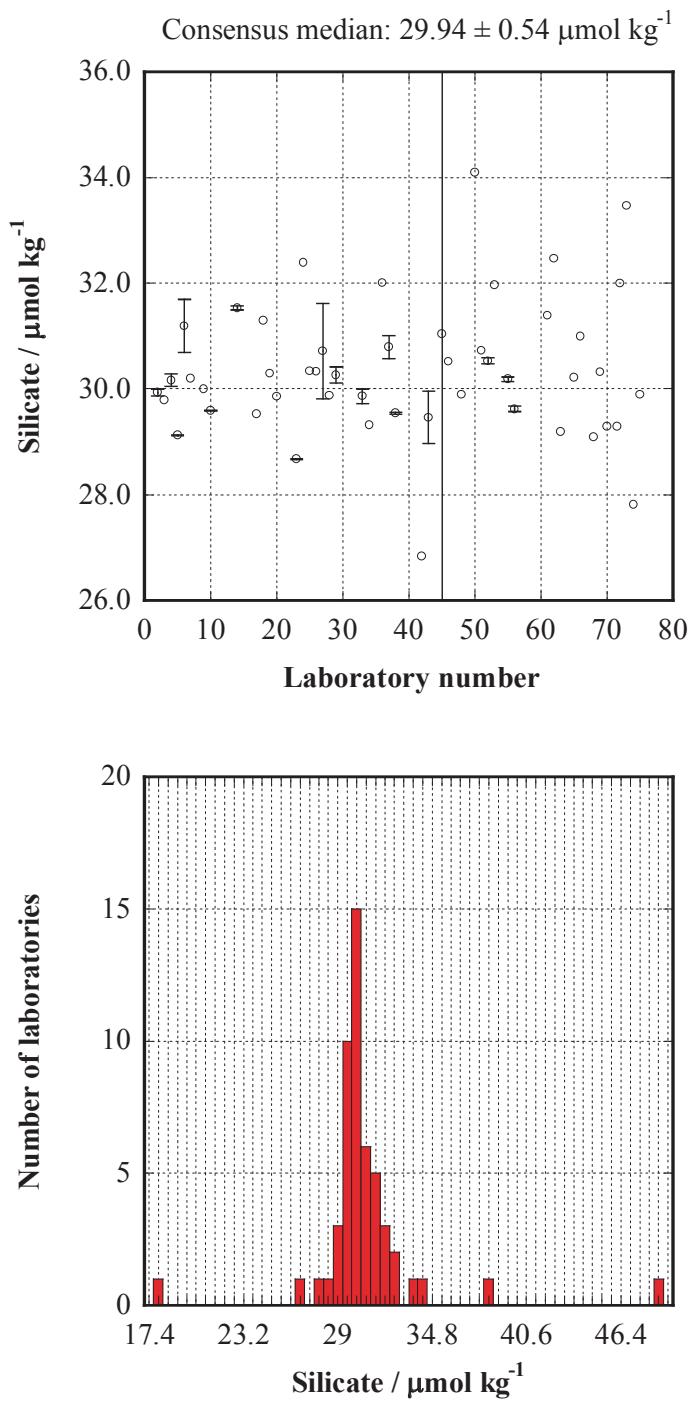
**Figure A5-4 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration of sample #4 (lower panel)**

## Sample 5 Silicate



**Figure A5-5 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #5 (lower panel)**

## Sample 6 Silicate



**Figure A5-6 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #6 (lower panel)**

## **Appendix IV**

**Documents related to 2008 inter-comparison study**



## IV-1 Call for participating

1 August 2008

Dear Colleague,

This letter is to invite you to the third “2008 Inter-comparison study of Reference Material of Nutrients (RMNS) in seawater”.

In 2003 Michio Aoyama, of the Meteorological Research Institute, Japan, organized an inter-comparison study which include 18 laboratories (Aoyama, 2006, Aoyama et. al, 2007). In 2006 Michio Aoyama organized second inter-comparison study which included 55 different laboratories world wide (Aoyama, 2008 in preparation). Both inter-comparison studies clearly show that global use of reference materials of nutrients in seawater would greatly improve the comparability of nutrients data in the world’s oceans. You will see results of these two inter-comparison studies via MRI’s web site.

<http://www.mri-jma.go.jp/Dep/ge/INSS.html>

In early 2007 Michio Aoyama had visited NOC in Southampton. One of the reasons for their visit was to discuss the results of the inter-calibration. This was extended to an invitation to the European participants in the inter-calibration and other interested nutrient chemists to attend a discussions meeting at NOC.

Following on from this an International Workshop on Chemical Reference Materials in Ocean Science was held in Tsukuba, Japan, on 29 October to 1 November 2007. It focused on the measurement of nutrients and of ocean CO<sub>2</sub> parameters, and the current status of available chemical reference materials, particularly for nutrient references in ocean science were discussed. The participants agreed to start a collaborative program, called the International Nutrients Scale System (INSS), with the aim to establish global comparability and traceability of nutrient data. The agreements at this workshop in Tsukuba 2007 marked an epoch in the history of nutrient comparability.

The “International Nutrients Scale System (INSS)” in seawater was agreed as the appropriate way to achieve this goal. In 2009 (Feb. 10th-12th) a second INSS international workshop will be held to discuss progress since 2007, and discuss future tasks. You will see details of 2009 INSS international workshop at [http://www.mri-jma.go.jp/Dep/ge/2009INSSworkshop/2009inss\\_workshop\\_index.html](http://www.mri-jma.go.jp/Dep/ge/2009INSSworkshop/2009inss_workshop_index.html), and a leaflet enclosed.

This “2008 Inter-comparison study of Reference Material of Nutrients (RMNS) in seawater” is planned to improve comparability of nutrient data as well as at the previous two inter-comparison studies and to exchange the knowledge of analytical method of nutrients in seawater in each laboratory. Therefore, if you join this inter-comparison study, you will be asked to report nutrients concentration in the samples and details of analytical method of nutrient in your laboratory. Results of this inter-comparison study would be also discussed in the 2009 INSS international workshop.

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

1. If you do not return the sheet by 15 September 2008, you will not receive any RMNS samples.
2. I will acknowledge receipt of your reply and list of the participants by 30 September 2008. If you do not receive an acknowledgement by 30 September 2008, please contact us in case your reply has gone elsewhere..
3. The reply sheet will confirm that your wish to participate this inter-comparison study and to analyzing the samples and submitting results before the reporting deadline, 15 January 2009, or returning the samples intact before the reporting deadline, if for any reason you are unable to analyze them. I expect to receive nutrients concentrations for nitrate, nitrite, phosphate and silicate. I also welcome to receive concentrations for ammonia, DOP and DON as optional.
4. Results reported will be published with the name of data originator after the data in the publication is confirmed by each data originator.

Best regards,

Michio AOYAMA, Dr.

Senior Scientist

Geochemical Res. Dep.

Meteorological Research Institute

e-mail: [maoyama@mri-jma.go.jp](mailto:maoyama@mri-jma.go.jp)

2008 Inter-comparison study of Reference Material of Nutrients (RMNS) in seawater

**IMPORTANT DATES**

DEADLINE OF REPLY: 15 SEPTEMBER 2008.

LIST OF PARTICIPANT: 30 SEPTEMBER 2008.

SAMPLES SHIPPED BY : 15 OCTOBER 2008

REPORTING DEADLINE: 15 JANUARY 2009

EXPECTED DRAFT OF INTERCOMPARISON SUMMARY:

10 FEBRUARY 2009 (at 2009 INSS International Workshop at Paris)

PLEASE RETURN THIS SHEET TO

Ms. Sachie ISHIKAWA at [kagaku28@mri-jma.go.jp](mailto:kagaku28@mri-jma.go.jp) by e-mail

or mail to

Michio AOYAMA

Geochemical Res. Dep.

Meteorological Res. Inst.

Nagamine 1-1

Tsukuba 305-0052

JAPAN

2008 Inter-comparison study of Reference Material of Nutrients (RMNS) in seawater

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

Name:

Affiliation:

Full postal address to receive samples

E-mail

Date:

Your comment:

**Note: You can download this format from**  
<http://www.mri-jma.go.jp/Dep/ge/RMNScomp2008.html>

## IV-2 Instructions for samples

6 Oct. 2008

31 Oct. 2008 add 7 and 8

## Instructions for samples

### 1. Package contents

- 1) Your package contains 6 bottles
- 2) You will see the sample IDs, from Sample1 to Sample6, and lab#.

### 2. Preparations of samples

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

### 3. Analyses

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

SAMPLE1	34.45+-0.01
SAMPLE2	34.27+-0.01
SAMPLE3	34.61+-0.01
SAMPLE4	34.62+-0.01
SAMPLE5	34.27+-0.01
SAMPLE6	34.63+-0.01
SAMPLE 7	34.34+-0.01
SAMPLE 8	34.59+-0.01

3) Maximum concentrations of the nutrients in the eight samples can be assumed as follows in micromoles per kilogram. These are the Pacific Ocean waters origin.

	Nitrite	Nitrate	Phosphate	Silicate
SAMPLES 1 to 6	<1.0	<45	<3.5	<170
SAMPLE 7	<1.0	<45	<3.5	between 220 and 270

SAMPLE 8            Ammonia concentration <6.0

#### 4. Reporting of results

- 1) Concentrations in micromoles per kilogram, alternatively in micromoles per liter with the ambient temperature during the analysis, should be reported using the reporting format which can be obtained from the website of this intercomparison at MRI.
- 2) Please report only one value for each parameter for each sample.
- 3) REPORTING DEADLINE: 15 January 2009

### IV-3 Follow-up survey for silicate standards

20 February 2009

Inter-laboratory Comparison for Reference Material for Nutrients in Seawater 2008:

Follow up survey on primary Silicate Standards

Dear Participant

Last week at the 2009 INSS International Workshop in Paris, ways were discussed of how the differences reported by different labs in the preliminary report of 2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater could be further investigated.

As you are aware one of the main reasons that has lead to need to develop RMNSs is that absolutely pure chemicals are not available for the calibration of nutrient analyses, and that this particularly true for the standards we use in the determination of silicate.

At the meeting Karel Bakker from the Royal Netherlands Institute for Sea Research (RNIOZ) suggested that he would be willing to do measurements to compare the concentration of silicate in the primary standards used by all the different labs in the 2008 inter-comparisons of RMNSs. The meeting agreed that this was an excellent suggestion that if carried out would help considerably in explaining the difference in the reported values

For this new exercise we need your further co-operation to carry out the following jobs:

1. Please e-mail Karel (Karel.Bakker@nioz.nl) as soon as possible to confirm that you are willing to send him a sample of your primary standard.
2. Please complete the attached information form (an example completed by RNIOZ is also attached) and return it by e-mail to Karel.
3. Karel will then send you container for the return of your sample. Please fill the sample vial and return it to RNIOZ using the included Address Sticker from the RNIOZ as soon as possible, along with a printed copy of your completed information form.

We look forward to your co-operation in what should be an enlightening extension to the 2008 inter-calibration exercise.

With our best regards

Michio Aoyama  
David Hydes  
Karel Bakker

**Follow up survey on primary silicate standards**

Information on Silicate stock solutions used for analysis.

<b>Lab name</b>	
<b>Lab postal address</b>	
<b>E-mail address</b>	
<b>Lab no. according to INSS rounds</b>	
<b>A: In case of weighing in Silica salt:</b>	
<b>Name of Silicate salt used</b>	
<b>Name of manufacturer of salt</b>	
<b>Purity of salt in %</b>	
<b>Manufacturer's Art no. and Lot no.</b>	
<b>Weight of Silica salt used to prepare standard</b>	
<b>Concentration of Silicate stock solution sent to RNIOZ (micro-Mol/Liter).</b>	
<b>B: In case of Stock solution from factory:</b>	
<b>Name of manufacturer of Silicate solution</b>	
<b>Manufacturer's Art no. and Lot no.</b>	
<b>Concentration of Silicate stock solution sent to RNIOZ (micro-Mol/Liter).</b>	
<b>General Information on working standards:</b>	
<b>Dilution of Silicate stock used in RMNS 2008</b>	
<b>Used diluents for preparation of working standard solutions, LNSW, DIW, or ASW. 1)</b>	
<b>Concentrations of highest Silicate calibration point in inter comparison 2008 in working standard (micro-Mol/Liter).</b>	
<b>Amount of any additives made to the stock solution (e.g. NaOH, HgCl<sub>2</sub>, or Chloroform).</b>	
<b>Analytical Method, Literature Reference</b>	
<b>1).</b> <b>LNSW; Low Nutrient Sea Water</b> <b>DIW; Deionised Water</b> <b>ASW; Artificial Sea Water</b>	

Procedure of filling provided container with stock solution:

1. Label container with lab.name and lab number used for INSS rounds
2. Rinse container 3 times with stock solution.
3. Fill container with stock solution using about 90% of the total volume of the provided container (leave 10% headspace in container).
4. Place the container in provided plastic bag. Fully seal the bag to prevent evaporation, and place the container plus bag and this information sheet in a suitable box.
5. Send the box to the address on the provided RNIOZ label, as soon as possible.

RNIOZ would like to measure all the Silicate stock solutions in one single run the second week of April 2009. Please return your sample before this date. The more samples that can be run at the same time the more reliable the results of this essential exercise will be. Samples returned at later date will of course still be measured but due to logistical constraints at RNIOZ it may not possible to do this until later in the year.



## **Appendix V**

### **History of nutrient inter-comparison studies**



## History of inter-laboratory nutrient comparison studies

This history of nutrient inter-laboratory comparison (I/C) studies is based on several reports of previous inter-comparison exercises. The histories of the first to fourth International Council for the Exploration of the Sea (ICES) exercises are derived from Aminot and Kirkwood's (1995) detailed report of the fifth ICES inter-comparison, which includes histories of the first to fourth ICES exercises. Histories of the fifth ICES exercise, the first and second NOAA/NRC I/C studies, and the MRI 2003 inter-comparisons are also summarized in Aoyama et al., 2008.

This history has been updated to reflect recent developments.

### 1. First ICES Exercise

The first inter-calibration study to include nutrients—Involving only Baltic nations—was in June 1965, when three research vessels met by private agreement in Copenhagen. The three vessels were:

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

For this experiment, each ship contributed freshly collected bulk samples, which were sub-sampled 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, in Leningrad, during the 5th Conference of Baltic Oceanographers; and Part II, in Copenhagen, at the 54th ICES Statutory Meeting.

#### Part I, Leningrad (May 1966)

The participating research vessels were:

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

The research vessels delivered bulk water samples, which were sub-sampled 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 determinants 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, 1965), 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 period 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 inter-comparison work on phosphate so far had consisted of simultaneous analysis of freshly obtained sub-samples by a small number of highly competent workers, in close contact with each other, exchanging calibration solutions, ideas, technical details, and other information. 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 (UNESCO, 1967) report, they announced: "There seems to be no need for any further intercalibration in the determination of inorganic phosphate by this method." However, with the advent of the autoanalyzer, the need for laboratory inter-calibration again became evident.

### **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 was an ambitious project.

Samples were distributed in 1969 and 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).

With this study, 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 of this study 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 with (identified) 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 tables of the results, but it was not possible to link them together. Hindsight suggests that this may have been counterproductive; there may be 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 data of poor quality.

#### 4. Fourth ICES Exercise

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

The fourth exercise differed from the third 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 inter-comparison 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 the identities of laboratories, their results, and a means for any reader to contact them.

Sixty-nine laboratories from 22 countries submitted results, and 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 measurements, a fifth ICES inter-comparison 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 inter-comparison study 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), and Turkey (1).

The method of sample preparation for the fifth inter-comparison-autoclaving-imposed constraints that resulted in there being only two relevant determinants per sample (nitrate and nitrite in one series; phosphate and ammonia in the other series). A large volume of low-nutrient natural seawater was spiked with known concentrations of nutrient salts. Although the concentrations in the distributed samples covered a greater concentration range than that in the fourth inter-comparison, the concentration levels were representative of the Atlantic Ocean: 1–26 µmol L<sup>-1</sup> for nitrate and 0.08–1.85 µmol L<sup>-1</sup> for phosphate. (Amiot and Kerouel, 1995)

There have been no further ICES inter-comparison exercises since 1993.

## 6. QUASIMEME

The European Union (EU) supported the QUASIMEME project between 1993 and 1995. The aim of this project was to develop a holistic quality-assurance programme for marine environmental monitoring information in Europe. As a result of this pioneering project, a marine network and laboratory performance studies have been established for most of the determinants measured in the EU marine environmental programmes for both monitoring and research purposes. The nutrient part of QUASIMEME was based entirely on the groundbreaking work of ICES experts, using the principles and methodologies described above. The project proved that laboratories that regularly followed the learning programmes and the laboratory testing schemes improved the quality of their data.

After the EU funding ended in 1995, the QUASIMEME scheme continued on a subscription basis. It is now possible for any laboratory worldwide to participate. QUASIMEME results have been used to assess the quality of data submitted to the marine conventions for the purpose of assessing the status of marine environmental quality.

## 7. 2000 NOAA/NRC Inter-comparison

In 2000, the National Oceanic and Atmospheric Administration (NOAA, USA) and the National Research Council of Canada (NRC) conducted an inter-comparison; distributing as a test material MOOS-1, a proposed certified reference material for nutrients in seawater (Clancy and Willie, 2004). The sample material was intended as 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 bottle. The prepared samples were sent to 36 participating laboratories. Thirty sets of results were returned.

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

## 8. 2002 NOAA/NRC Inter-comparison

In 2002, NOAA/NRC undertook a further inter-comparison exercise to assess the current capabilities of a group of laboratories to quantitate orthophosphate, silicate, nitrite, and nitrate+nitrite in a seawater sample. This was the second such exercise sponsored by the NOAA Center for Coastal Monitoring and Assessment (CCMA) and coordinated by the Institute for National Measurement Standards of the NRC of Canada. Two seawater samples—one from Pensacola Sound (Florida, USA) 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 (2000) NOAA/NRC inter-comparison exercise had been overcome, although the orthophosphate data indicated a larger inter-laboratory spread of results than expected.

Results for silicate, nitrite, and nitrate+nitrite in the distributed seawater samples were acceptable for the majority of the participants, and generally deviated less than  $\pm 10\%$  from the assigned mean.

## 9. 2003 MRI Inter-comparison

For the 2003 MRI inter-comparison study, samples were prepared from autoclaved natural seawater. Sample homogeneity was confirmed by repeatability of measurements. Sets of 6 samples were distributed, covering a concentration range greater than that in previous I/C studies. The concentrations were  $0\text{--}38 \mu\text{mol kg}^{-1}$  for nitrate,  $0\text{--}0.9 \mu\text{mol kg}^{-1}$  for nitrite,  $0\text{--}2.7 \mu\text{mol kg}^{-1}$  for phosphate, and  $0\text{--}136 \mu\text{mol kg}^{-1}$  for silicate. 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 the homogeneities for phosphate and more than 10 times those for phosphate and silicate. For nitrate, the standard deviations were only about double the homogeneities. These results indicated that variability between in-house standards at the participating laboratories, rather than analytical precision, was the primary source of inter-laboratory discrepancy. Therefore, the use of a certified RMNS would be essential for establishing nutrient data sets that could be compared across laboratories, especially for silicate and phosphate. (Aoyama, 2006)

## 10. 2006 MRI Inter-comparison

In the 2006 MRI inter-comparison study, autoclaved natural seawater was used as a reference material for nutrients in seawater, similar to the 2003 inter-comparison. Sample homogeneity was confirmed by repeatability of measurement, and homogeneities for nitrate, phosphate, and silicate were 0.2%, 0.3%, and 0.2%, respectively. Sets of 6 samples were prepared covering a concentration range of 0.1–42.4  $\mu\text{mol kg}^{-1}$  for nitrate, 0.0–0.6  $\mu\text{mol kg}^{-1}$  for nitrite, 0.0–3.0  $\mu\text{mol kg}^{-1}$  for phosphate, and 1.7–156.1  $\mu\text{mol kg}^{-1}$  for silicate. A total of 55 sets of samples were distributed to 55 laboratories in 20 countries. Results were returned by 52 laboratories in 19 countries. (Aoyama et al., 2008)

## 11. 2008 MRI Inter-comparison

In 2008, MRI supervised another inter-comparison study using autoclaved natural seawater as a reference material for nutrients in seawater, just as in 2003 and 2006. A total of 58 sets of 6–8 samples were distributed to 58 laboratories in 20 countries. Results were returned by 52 laboratories in 19 countries.

Two of the six samples used in the 2008 inter-comparison study were from the same batches used in the 2006 study. This permitted the determination of the internal comparability at each laboratory that participated in both the 2006 and 2008 studies, as well as the international comparability of the nutrient data among the participating laboratories.

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