Appendix I

List of participating laboratories

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

Table A1 – List of participating laboratories

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

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

Lah#	RMNS Inter-comparison study
Lao#	2003*
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Table A2Cross reference table of lab# between 2006 I/C in and 2003 I/C

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\* : Laboratory# of 2003 Inter-comparison study

Appendix II

**Results submitted by participating laboratories** 

Table A	3. Res	ults	repo	orted by	the pai	rticipar	nts									2006	<b>RMNS Int</b>	tercompar	ison Exe	rcise
LAB SAMP	LE YEAR	MOR	V DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	XON	err	Flag	reduct	Silicate	err	Flag
-																				
-	2006	12	Ξ	22	0.51	0.01	2	0.63	0.01	2	5.74		2	6.38	0.22	2		30.5	0.60	2
2	2006	12	Ħ	22	2.76	0.23	2	0.14	0.01	2	33.9		2	34.1	0.09	2		159.4	1.64	2
e	2006	12	Ξ	22	2.99	0.11	2	<0.08		5	43.2		2	43.2	0.12	2		136.2	2.24	2
4	2006	12	Ξ	22	1.65	0.16	2	0.36	0.01	2	22.6		2	23.0	1.43	2		59.8	1.46	2
Q	2006	12	Ξ	22	0.06	0.01	2	<0.08		5	<0.08		Q	<0.08		2		1.46	0.07	2
9	2006	12	Ξ	22	1.65	0.16	2	0.38	0.01	2	22.1		2	22.5	0.62	2		59.7	1.81	2
2																				
-	2006	Ξ	4	26.9	0.46	0.00	2	0.59	0.00	2			6	6.19	0.03	2				6
2	2006	Ξ	4	26.9	2.54	0.00	2	0.09	0.00	2			6	33.05	0.03	2				6
З	2006	Ξ	4	26.9	3.08	0.00	2	0.00	0.00	2			6	41.25	0.03	2				6
4	2006	Ξ	4	26.9	1.60	0.00	2	0.33	0.00	2			6	21.86	0.03	2				6
2	2006	Ξ	4	26.9	0.02	0.00	2	0.00	0.00	2			6	0.01	0.03	2				6
9	2006	1	4	26.9	1.59	0.00	2	0.33	0.00	2			6	21.93	0.03	2				6
e																				
-	2006	Ξ	22	23.5	0.51	0.02	2	0.61	0.01	2	5.67	0.05	2	6.28	0.05	2	98.6	31	0.1	2
2	2006	Ξ	22	23.5	2.54	0.02	2	0.09	0.01	2	33.28	0.05	2	33.37	0.05	2	98.6	159	0.1	2
С	2006	Ξ	22	23.5	3.04	0.02	2	0.00	0.01	2	42.08	0.05	2	42.08	0.05	2	98.6	139.8	0.1	2
4	2006	Ξ	22	23.5	1.62	0.02	2	0.33	0.01	2	21.55	0.05	2	21.88	0.05	2	98.6	60.2	0.1	2
5	2006	Ξ	22	23.5	0.05	0.02	2	0.01	0.01	2	0	0.05	2	0.01	0.05	2	98.6	2.3	0.1	2
9	2006	Ξ	22	23.5	1.62	0.02	2	0.34	0.01	2	21.58	0.05	2	21.92	0.05	2	98.6	09	0.1	2
4																				
-	2006	6	25	23	0.47	0.004	9	0.63	0.01	9	5.97	0.04	9	9.9	0.04	9	100	30.82	0.23	9
2	2006	6	25	23	2.53	0.01	9	0.1	0.004	9	34.89	0.23	9	34.99	0.23	9	100	157.33	1.69	9
S	2006	6	25	23	3.06	0.01	9	0.02	0.004	9	44.13	0.4	9	44.15	0.03	9	100	137.52	0.95	9
4	2006	6	25	23	1.64	0.01	9	0.34	0.004	9	22.63	0.21	9	22.98	0.2	9	100	59.96	0.42	9
5	2006	6	25	23	0.02	0.004	9	0.02	0.00	9	0	0	9	0	0	9	100	1.6	0.02	9
9	2006	6	25	23	1.59	0.01	9	0.35	0.004	9	22.76	0.07	9	23.11	0.07	9	100	61.37	0.39	9
5																				
-	2006	12	9		0.470	0.01	2	0.614	0.01	2	5.557	0.014	2	6.171	0.014	2		31.613	0.152	2
2	2006	12	9		2.464	0.009	2	0.107	0.001	2	33.172	0.087	2	33.279	0.087	2		162.130	0.046	2
S	2006	12	9		2.972	0.010	2			5	42.365	0.071	2	42.365	0.071	2		141.881	0.079	2
4	2006	12	9		1.554	0.004	2	0.348	0.001	2	21.201	0.048	2	21.541	0.048	2		62.179	0.484	2
5	2006	12	9				5			5			5			5		1.941	0.008	2
9	2006	12	9		1.547	0.006	2	0.344	0.004	2	21.213	0.059	2	21.557	0.059	2		62.420	0.927	2
Flag 2:	accept	able	measu	<i>irement</i> ,	3: questi	onable,	4: bad,	5: below d	etction li	mit, 6: r	mean of rep	licate m	easurem	ent, 9: noi	t reporte	p				ĺ

Table A	3. (Co	ntinue	(pe												2006	<b>RMNS Int</b>	ercompar	ison Exe	ercise
LAB SAMP	LE YEAR	NOW	DAY TEMP	Phosphat	e err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
9																			č.
-	2006	11 16	3 22	0.40	0.04	9			6			6	5.2	0.1	9		28.4	0.6	9
2	2006	11 16	3 22	2.47	0.08	9			6			6	32.2	0.6	9		155.2	7.8	9
e	2006	11 16	3 22	3.06	0.09	9			6			6	41.4	0.8	9		134.0	6.7	9
4	2006	11 16	5 22	1.52	0.06	9			6			6	19.8	0.4	9		57.8	1.2	9
5	2006	11 16	5 22	0.00	0.03	9			6			6	0.0	0.1	9		1.5	0.0	9
9	2006	11 16	5 22	1.51	0.06	9			6			6	20.3	0.4	9		57.5	1.2	9
7																			
-	2006	10 3		0.49	0.005	2	0.626	0.005	2	5.58	0.05	2	6.21	0.05	2		30.2	0.1	2
2	2006	10 3		2.49	0.01	2	0.095	0.003	2	33.2	0.1	2	33.3	0.1	2		157	-	2
e	2006	10 3		2.97	0.01	2	0.012	0.003	2	42.0	0.1	2	42.0	0.1	2		136	-	2
4	2006	10 3	_	1.59	0.01	2	0.357	0.005	2	21.3	0.1	2	21.7	0.1	2		59.4	0.2	2
5	2006	10 3	_	0.030	0.004	2	0.018	0.003	2	0.04	0.03	2	0.06	0.03	2		1.69	0.05	2
9	2006	10 3	_	1.59	0.01	2	0.357	0.005	2	21.3	0.1	2	21.7	0.1	2		59.5	0.1	2
6																			
-	2006	11 1(	0	0.77		2	0.650		2	7.14		2	7.78		2		34.88		2
2	2006	11 1(	0	3.04		2	0.113		2	36.39		2	36.50		2		169.95		2
3	2006	11 1(	0	3.60		2	0.015		2	46.02		2	46.04		2		144.39		2
4	2006	11 1(	0	2.02		2	0.365		2	24.31		2	24.68		2		66.98		2
5	2006	11 1(	0	0.26		2	0.015		2	0.22		2	0.24		2		4.26		2
9	2006	11 1(	0	1.96		2	0.350		2	23.97		2	24.32		2		65.62		2
10																			
-	2006	10 5		0.48	0.03	9	0.72	0.02	9	5.4	0.2	9			6	>98.5	30.0	0.2	9
2	2006	10 5		2.45	0.04	9	0.11	0.01	9	33.3	0.3	9			6	>98.5	156.4	0.5	9
e	2006	10 5		2.95	0.03	9	0.02	0.01	9	42.0	0.4	9			6	>98.5	136.3	0.4	9
4	2006	10 5		1.57	0.03	9	0.40	0.01	9	21.4	0.2	9			6	>98.5	59.5	0.2	9
5	2006	10 5		0.03	0.02	9	0.02	0.01	9	0.0	0.0	9			6	>98.5	1.5	0.2	9
9	2006	10 5		1.57	0.03	9	0.40	0.01	9	21.4	0.3	9			6	>98.5	59.6	0.2	9
=																			
-	2006	10 1	25	0.40	0.01	2	0.65	0.00	2	5.79	0.03	2	6.44	0.03	2	100			6
2	2006	10 1	25	2.51	0.02	2	0.09	0.00	2	33.98	0.05	2	34.07	0.05	2	100			6
3	2006	10 1	25	3.05	0.01	2	0.01	0.00	2	42.70	0.08	2	42.71	0.08	2	100			6
4	2006	10 1	25	1.53	0.01	2	0.35	0.00	2	22.09	0.10	2	22.44	0.10	2	100			6
2	2006	10 1	25	0.01	0.01	2	0.01	0.00	2	0.00	0.02	2	0.01	0.02	2	100			6
9	2006	10 1	25	1.55	0.01	2	0.36	0.00	2	22.05	0.05	2	22.40	0.05	2	100			6
Flag 2:	accept	able m	easurement	: 3: que	stionable,	4: bad,	5: below o	etction li	mit, 6: n	rean of rep	dicate m	easureme	ent, 9: not	t reporte	0				Ĩ

Table A:	3. (Co	ntin	(panu													2006	<b>RMNS Int</b>	ercompari	son Exe	rcise
LAB SAMP	LE YEAF	S MO	N DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
12																				Ì
-	2006	6	22	20	0.45	0.04	2	0.53	0.04	2	5.0	0.4	2	5.5	0.4	2		29.0	0.2	2
2	2006	6	22	20	2.31	0.04	2	0.08	0.04	2	32.2	0.4	2	32.3	0.4	2		151.7	0.2	2
3	2006	6	22	20	2.81	0.04	2			5	41.2	0.4	2	41.3	0.4	2		131.9	0.2	2
4	2006	6	22	20	1.50	0.04	2	0.29	0.04	2	20.4	0.4	2	20.7	0.4	2		57.5	0.2	2
5	2006	6	22	20			5			5			5			5		1.3	0.2	2
9	2006	6	22	20	1.48	0.04	2	0.29	0.04	2	20.4	0.4	2	20.7	0.4	2		56.8	0.2	2
13																				
-	2006	10	Ξ	22.9	0.42	0.01	2	0.63	0.00	2	5.75	0.00	2	6.37	0.00	2	66			6
2	2006	10	Ξ	22.9	2.46	0.01	2	0.09	0.00	2	33.77	0.02	2	33.86	0.02	2	66			6
З	2006	10	Ξ	22.9	2.97	0.01	2	0.00	0.00	2	42.48	0.03	2	42.48	0.03	2	66			6
4	2006	10	Ξ	22.9	1.53	0.01	2	0.34	0.00	2	21.82	0.00	2	22.16	0.01	2	66			6
5	2006	10	Ξ	22.9	0.00	0.00	2	0.01	0.00	2	00.0	0.00	2	00.0	0.00	2	66			6
9	2006	10	=	22.9	1.52	0.01	2	0.35	0.00	2	21.83	0.01	2	22.18	0.01	2	66			6
14																				
-	2006	12	14		0.52	0.02	2	0.59	0.00	2			6	5.18	0.01	2		30.08	0.05	2
2	2006	12	14		2.52	0.02	2	0.09	0.00	2			6	29.37	0.10	2		158.95	0.00	2
3	2006	12	14		2.81	0.02	2	0.42	0.00	2			6	36.02	0.00	2		138.49	0.44	2
4	2006	12	14		1.56	0.02	2	0.34	0.01	2			6	17.32	0.08	2		61.60	0.00	2
5	2006	12	14		0.065	0.005	2	0.01	0.00	2			6	0.02	0.00	2		1.82	0.00	2
9	2006	12	14		1.56	0.01	2	0.35	0.00	2			6	17.46	0.05	2		61.46	0.05	2
15																				
-	2006	10	23-2	7	0.50	0.01	9	0.64	0.01	9	5.67	0.06	9	6.31	0.06	9		29.91	0.29	9
2	2006	10	23-2	7	2.60	0.04	9	0.10	0.00	9	33.27	0.47	9	33.38	0.47	9		152.1	2.8	9
3	2006	10	23-2	7	3.12	0.05	9	0.02	0.00	9	41.99	0.49	9	42.01	0.49	9		132.9	1.5	9
4	2006	9	23-2	7	1.65	0.02	9	0.35	0.01	9	21.31	0.18	9	21.66	0.18	9		57.2	1.3	9
5	2006	9	23-2	7	0.03	0.01	9	0.01	0.01	9	0.06	0.01	9	0.07	0.01	9		1.79	0.04	9
9	2006	10	23-2	7	1.66	0.03	9	0.36	0.01	9	21.24	0.11	9	21.60	0.11	9		57.3	0.71	9
16																				
-	2006	10	12	20	0.4693	0.0043	9	0.6183	0.0026	9	5.5092	0.0261	9	6.1274	0.0279	9	96	29.7157	0.0873	9
2	2006	10	12	20	2.6138	0.0168	9	0.0824	0.0082	9	33.6267	0.1461	9	33.7091	0.1497	9	96	154.4801	0.2336	9
3	2006	10	12	20	3.1759	0.0146	9	0.0005	0.0037	9	42.9368	0.1761	9	42.9310	0.1734	9	96	134.7864	0.2239	9
4	2006	10	12	20	1.6933	0.0017	9	0.3323	0.0018	9	21.7138	0.1117	9	22.0461	0.1120	9	96	58.9895	0.0463	9
5	2006	10	12	20	7600.0	0.0069	9	0.0043	0.0143	9	0.0375	0.0332	9	0.0418	0.0417	9	96	1.6053	0.0265	9
9	2006	10	12	20	1.7012	0.0051	9	0.3345	0600.0	9	21.6510	0.0635	9	21.9854	0.0699	9	96	58.7561	0.2441	9
Flag 2:	accept	table	meas	urement	3: quest	ionable,	4: bad,	5: below de	station lir	nit, 6: r	mean of rep	licate me	asurem	ent, 9: noi	: reported					

Table A	13. (Col	ntinue	(p													2006	<b>RMNS Int</b>	tercompari	ison Exe	rcise
I A SA	WPLE YEA	NOW AN	DAY T	EMP P	hosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
17																				
0.51	1 200	6 10	16	-	0.5099	0.0156	2	0.6455	0.0018	2	6.0181		2	6.6637	0.1119	2		31.7353	0.4674	2
	2 200	6 10	16		2.5555	0.0185	2	0.1055	0.0012	2	35.3625		2	35.4680	0.1288	2		163.3687	0.0893	2
	3 200	6 10	16		3.0876	0.0100	2	0.0205	0.0044	2	44.7860		2	44.8066	0.1800	2		142.1318	0.0923	2
	4 200	6 10	16		1.6585	0.0124	2	0.3585	0.0029	2	22.9179		2	23.2764	0.1880	2		62.2116	0.0895	2
0.00	5 200	6 10	16		0.0261	0.0033	2	0.0101	0.0020	2	0.1084		2	0.1185	0.0014	2		1.7252	0.1696	2
-	6 200	6 10	16		1.6385	0.0130	2	0.3546	0.0014	2	22.6693		2	23.0240	0.1164	2		62.0710	0.1495	2
18																				
8097	1 200	6 11	23		0.51		2	0.61		2	5.51		2	6.12		2		30.3		2
0778	200	6 11	23		2.47		2	0.08		2	33.4		2	33.5		2		158		2
	3 200	6 11	23		2.95		2	0.03		2	42.2		2	42.3		2		137		2
	4 200	6 11	23		1.6		2	0.33		2	21.6		2	22.0		2		59.6		2
	5 200	6 11	23		0.04		2	0		2	0		2	0		2		1.77		2
	6 200	6 11	23		1.59		2	0.32		2	21.7		2	22.1		2		59.6		2
19																				
386	1 200	6 11	23	-	0.55	0.02	2	0.62	0.01	2	5.95	0.1	2	6.57	0.1	2		31.6	0.1	2
120	200	6 11	23		2.54	0.02	2	0.09	0.01	2	34.7	0.1	2	34.8	0.1	2		161	F-	2
90. T.	3 200	6 11	23		3.07	0.02	2	0.00	0.01	2	43.7	0.1	2	43.7	0.1	2		140	-	2
	4 200	6 11	23		1.58	0.02	2	0.34	0.01	2	22.2	0.1	2	22.6	0.1	2		60.7	0.1	2
1000	5 200	6 11	23		0.06	0.02	2	0.00	0.01	2	0.09	0.1	2	0.09	0.1	2		1.87	0.1	2
	6 200	6 11	23		1.58	0.02	2	0.34	0.01	2	22.4	0.1	2	22.8	0.1	2		60.5	0.1	2
20																				
2005	1 200	6 11	16-21	9.4	0.52	0.02	2	0.56	0.01	2	6.05		2	6.61	0.07	2	102	28.36	1.43	2
174.3	2 200	6 11	16-21	9.4	2.58	0.02	2	0.02	0.01	2	24.15		2	24.17	0.05	2	102	149.27	1.45	2
	3 200	6 11	16-21	9.4	3.08	0.02	2			2	24.50		2	24.50	0.04	2	102	132.86	0.03	2
	4 200	6 11	16-21	9.4	1.63	0.04	2	0.27	0.00	2	19.96		2	20.23	0.10	2	102	58.69	1.20	2
	5 200	6 11	16-21	9.4	0.08	0.02	2			5	00.00		2			2	102	1.50	0.01	2
	6 200	6 11	16-21	9.4	1.64	0.02	2	0.27	0.00	2	19.85		2	20.12	0.04	2	102	57.72	0.52	2
23																				
	-			-	0.46	0.02	2	0.67	0.05	2	9	0.1	2			6		28.8	0.1	2
	2				2.55	0.03	2	0.14	0.03	2	33.8	0.8	2			6		155.3	0.3	2
	3				3.09	0.02	2	0.05	0.01	2	41.7	1.2	2			6		134.8	0.4	2
	4				1.64	0.03	2	0.42	0.01	2	21.9	0.9	2			6		58	0.3	2
	2				0.04	0.03	2	0.04	0.01	2	<dl< td=""><td></td><td>5</td><td></td><td></td><td>6</td><td></td><td>1.25</td><td>0.02</td><td>2</td></dl<>		5			6		1.25	0.02	2
	9				1.69	0.03	2	0.43	0.02	2	21.9	0.8	2			6		58.1	0.4	2
Hag	2: accel	otable r	neasure	ment	3: questi	onable,	4: bad,	5: below d	etction lir	mit, 6:	mean of rep	licate r	neasurem	ent, 9: not	: reported	-				

Table A	3. (Co	ntinuea	0												2006 RI	ANS Intel	rcompari	son Exe	rcise
LAB SAMF	PLE YEAF	MON D	AY TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	XON	err	Flag re	duct S	Silicate	err	Flag
24																			ĺ
-	2006	10 5	25.8	0.58		2	0.61		2	5.83	0.01	2	6.70	0.01	2		31.7		2
2	2006	10 5	25.8	2.52		2	0.10		2	32.88	0.08	2	33.02	0.08	2		145.3	0.5	2
Э	2006	10 5	25.8	3.03		2	0.01		2	41.24	0.09	2	41.25	0.09	2		167.9	0.2	2
4	2006	10 5	25.8	1.74		2	0.35		2	21.48	0.05	2	21.97	0.05	2		63.3		2
5	2006	10 5	25.8	0.06		2	0.02		2	0.00	0.00	2	00.0	0.00	2		2.3		2
9	2006	10 5	25.8	1.69		2	0.35		2	21.65	0.07	2	22.15	0.07	2		63.1		2
25																			
-	2006	12 12	21.8	0.474 (	0.02	2	0.626	0.015	2	5.56	0.26	2	6.19	0.25	2 99		29.36	0.5	2
2	2006	12 12	21.8	2.509 (	0.02	2	0.105	0.015	2	33.35	0.26	2	33.46	0.25	2 99	-	156.3	1.0	2
3	2006	12 12	21.8	3.018 0	0.02	2	0.022	0.015	2	42.24	0.26	2	42.27	0.25	2 99		134.5	1.0	2
4	2006	12 12	21.8	1.554 0	0.02	2	0.351	0.015	2	21.46	0.26	2	21.81	0.25	2 99		58.23	0.5	2
5	2006	12 12	21.8	0.020 (	0.02	2	0.022	0.015	2	0.03	0.26	2	0.05	0.25	2 99		1.47	0.5	2
9	2006	12 12	21.8	1.588 (	0.02	2	0.356	0.015	2	21.44	0.26	2	21.8	0.25	2 99		58.19	0.5	2
26																			
-	2006	12 22		0.44 (	00.0	2	0.64	0.00	2	5.68	0.04	2	6.32	0.04	2		28.99	0.19	2
2	2006	12 22		2.48 (	0.01	2	0.11	0.00	2	33.48	0.04	2	33.59	0.04	2		155.64	0.14	2
З	2006	12 22		3.04 0	00.0	2	0.02	0.00	2	42.51	0.04	2	42.54	0.04	2		135.89	0.38	2
4	2006	12 22		1.52 (	00.0	2	0.37	0.00	2	21.45	0.01	2	21.82	0.01	2		58.38	0.21	2
5	2006	12 22		0.02 (	0.01	2	0.03	0.00	2	0.09	0.00	2	0.12	0.00	2		1.10	0.16	2
9	2006	12 22		1.50 (	0.02	2	0.37	0.00	2	21.34	0.03	2	21.71	0.03	2		58.52	0.25	2
27																			
-	2006	11 15		0.46 (	0.05	2			6			6	6.41	0.05	2		38.4	0.8	2
2	2006	11 15		2.28 (	0.20	2			6			6	34.1	0.6	2		152	-	2
З	2006	11 15		2.76 (	0.16	2			6			6	42.7	0.5	2		134	-	2
4	2006	11 15		1.41 (	0.19	2			6			6	22.6	0.5	2		58.6	0.7	2
5	2006	11 15		0.15 (	70.0	2			6			6	0.36	0.05	2		3.37	0.26	2
9	2006	11 15		1.41 (	0.20	2			6			6	22.6	0.5	2		58.5	0.6	2
28																			
-	2006	10 18		0.33 (	0.02	2	0.57	0.03	2	4.04	0.18	2	4.60	0.21	2				6
2	2006	10 18		2.56 (	0.12	2	0.10	0.00	2			6			6				6
3	2006	10 18		3.02	0.14	2			6			6			6				6
4	2006	10 18		1.51 (	0.07	2	0.26	0.01	2	20.78	0.95	2	21.04	0.96	2				6
Q	2006	10 18				6			6	1.30	0.06	2	1.30	0.06	2				6
9	2006	10 18		1.52 (	0.07	2	0.25	0.01	2	20.55	0.94	2	20.81	0.95	2				6
Flag 2	: accept	table me	asurement,	3: questic	mable,	4: bad,	5: below d	etction li	mit, 6: n	rean of rep	licate m	easurem	ent, 9: no	treporte	q				1

Table A	3. (Co	intir	(panu													2006	RMNS Int	ercompari	ison Exe	rcise
LAB SAMF	LE YEAR	S MO	N DAY	TEMP F	<sup>o</sup> hosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag 1	reduct	Silicate	err	Flag
29																				
-	2006	10	24	23.5	0.46	0.01	2	0.61	0	2	5.93	0.02	2	6.54	0.02	2	100	31.73	0.01	2
2	2006	10	25	22.6	2.52	0	2	0.09	0	2	33.54	0.03	2	33.62	0.02	2	100	156.62	0.14	2
e	2006	10	25	23	3.02	0	2	0	0	2	41.91	0.03	2	41.92	0.02	2	100	136.66	0.02	2
4	2006	10	26	24.9	1.57	0	2	0.34	0	2	21.96	0.02	2	22.3	0.02	2	100	62.22	0.17	2
5	2006	10	26	26.2	0.01	0.01	2	0	0	2	0	0.01	2	0	0.01	2	100	2.05	0.03	2
9	2006	10	27	25.1	1.58	0.01	2	0.34	0	2	21.99	0.03	2	22.33	0.03	2	100	61.58	0.03	2
30																				
-	2006	Ξ	7	20.6	0.46	0.00	2	0.63	0.01	2	5.64	0.05	2	6.27	0.05	2		27.5	0.1	2
2	2006	Ξ	8	21.8	2.29	0.01	2	0.10	0.00	2	33.61	0.09	2	33.71	0.09	2		166.1	0.7	e
3	2006	Ξ	8	21.8	2.75	0.03	2	0.01	0.00	2	42.23	0.11	2	42.24	0.11	2		139.5	0.5	3
4	2006	Ξ	œ	19.6	1.48	0.01	2	0.37	0.00	2	21.91	0.18	2	22.28	0.18	2		63.4	0.0	e
5	2006	Ξ	7	20.6	0.06	0.01	2	0.02	0.00	2	0.09	0.00	2	0.11	0.00	2		1.5	0.0	2
9	2006	=	8	21	1.46	0.01	2	0.36	0.00	2	22.12	0.02	2	22.48	0.02	2		63.7	0.3	з
31																				
-	2006	=	2		0.42		2	0.58		2	5.36		2	5.94		2		30.1		2
2	2006	11	2		2.75		2	0.093		2	32.9		2	33.0		2		153		2
S	2006	11	2		3.29		2			5	41.2		2	41.3		2		133		2
4	2006	Ħ	2		1.66		2	0.34		2	20.7		2	21.0		2		57.7		2
Q	2006	11	2		0.03		2			5	0.78		2	0.80		2		1.70		2
9	2006	Ξ	2		1.63		2	0.35		2	20.6		2	20.9		2		57.2		2
32																				
-	2006	Ξ	15	20	1.03	0.10	2	0.64	0.21	2	4.72	0.16	2	5.36	0.37	2				6
2	2006	Ξ	15	20	3.08	0.10	2	0.21	0.21	2	31.49	0.16	2	31.71	0.37	2				6
c	2006	Ξ	15	20	3.08	0.10	2	0.21	0.21	2	28.34	0.16	2	28.55	0.37	2				6
4	2006	Ξ	15	20	1.03	0.10	2	0.42	0.21	2	18.89	0.16	2	19.32	0.37	2				6
5	2006	Ξ	15	20	0.00	0.10	2	0.00	0.21	2	1.57	0.16	2	1.57	0.37	2				6
9	2006	Ξ	15	20	1.03	0.10	2	0.42	0.21	2	18.89	0.16	2	19.32	0.37	2				6
33																				
-	2006	6	18		0.53	0.01	9	0.63	0.00	9	5.69	0.04	9	6.32	0.04	9		29.64	0.09	9
2	2006	6	18		2.57	0.03	9	0.14	0.00	9	33.70	0.09	9	33.84	0.08	9		155.17	0.44	9
3	2006	6	18		3.04	0.04	9	0.06	0.00	9	42.51	0.34	9	42.57	0.33	9		134.44	1.23	9
4	2006	6	18		1.55	0.02	9	0.36	0.00	9	21.73	0.13	9	22.09	0.13	9		59.21	0.62	9
2	2006	6	18		0.09	0.005	9	0.06	0.00	9	0.10	0.03	9	0.16	0.03	9		1.81	0.06	9
9	2006	6	18		1.56	0.02	9	0.36	0.00	9	21.58	0.02	9	21.94	0.02	9		58.59	0.03	9
Hag 2	accept	table	s meas	urement	3: questi	ionable,	4: bad, !	5: below d	etction li	mit, 6: m	rean of rep	licate m	easureme	int, 9: not	reported	~				

Table A	3. (Col	ntin	(pan													2006	<b>RMNS Int</b>	tercompar	ison Exe	ercise
LAB SAMP	LE YEAR	MON	N DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
34																				Ĩ
-	2006	6	25	20.5	0.28	0.02	2	0.66	0.01	2	5.61	0.01	2	6.29	0.02	2	96	30.33	0.22	2
2	2006	6	25	20.5	2.26	0.05	2	0.13	0.01	2	33.03	0.02	2	33.17	0.03	2	96	155.76	0.62	2
S	2006	6	25	20.5	2.85	0.07	2	0.05	0.01	2	41.94	0.02	2	41.99	0.03	2	96	136.00	1.09	2
4	2006	6	25	20.5	1.42	0.05	2	0.38	0.01	2	21.64	0.04	2	22.04	0.05	2	96	59.90	0.42	2
5	2006	6	25	20.5	0.06	0.05	2	0.07	0.02	2	0.02	0.01	2	0.05	0.02	2	96	1.96	0.05	2
9	2006	6	25	20.5	1.38	0.04	2	0.39	0.00	2	21.61	0.08	2	22.02	0.08	2	96	59.59	0.33	2
35																				
-	2006	Ξ	13		0.48	0.05	2	0.68	0.01	2			6	6.56	0.40	2		30.14	0.39	2
2	2006	Ξ	13		2.71	0.05	2	0.11	0.01	2			6	34.23	0.18	2		141.03	1.78	2
S	2006	Ξ	13		3.25	0.03	2	0.013	0.006	2			6	43.31	0.71	2		133.22	1.39	2
4	2006	Ξ	13		1.73	0.03	2	0.37	0.01	2			6	23.08	0.85	2		58.78	0.99	2
2	2006	1	13		0.12	0.01	2	0.016	0.006	2			6	0.21	0.04	2		1.32	0.02	2
9	2006	Ξ	13		1.70	0.06	2	0.39	0.01	2			6	23.20	0.49	2		58.59	0.57	2
36																				
-	2006	12	15		0.54		2	09.0		2	5.97		2			6		27.82		2
2	2006	12	15		2.88		2	0.11		2	34.76		2			6		155.59		2
ŝ	2006	12	15		3.51		2	0.03		2	41.84		2			6		137.21		2
4	2006	12	15		1.76		2	0.34		2	21.58		2			6		58.95		2
5	2006	12	15		0.05		2	0.01		2	0.18		2			6		2.48		2
9	2006	12	15		1.76		2	0.34		2	21.72		2			6		58.93		2
37																				
-	2006	12	5	30	0.49	0	9	0.69	0	9	5.35	0.02	9	6.03	0.02	9	100	27.39	0.02	9
2	2006	12	5	30	2.65	0.01	9	0.11	0.01	9	33.87	0.1	9	33.97	0.1	9	100	145.72	0.23	9
3	2006	12	5	30	3.2	0	9	0	0	9	43.38	0.12	9	43.38	0.12	9	100	127.18	0.16	9
4	2006	12	5	30	1.69	0.01	9	0.37	0	9	21.41	0.06	9	21.78	0.06	9	100	55.3	0.17	9
2	2006	12	5	30	0.01	0.01	9	0	0	9	0.01	0.02	9	0.01	0.02	9	100	0.83	0.08	9
9	2006	12	5	30	1.68	0.01	9	0.37	0.01	9	21.4	0.02	9	21.76	0.02	9	100	54.79	0.04	9
38																				
-	2006	10	21	26.4	0.523		2	0.62		2	5.58		2	6.20		2		9.53		2
2	2006	10	21	26.4	2.523		2	0.09		2	33.28		2	33.37		2		154.33		2
3	2006	10	21	26.4	3.018		2	0.01		2	42.26		2	42.27		2		133.98		2
4	2006	10	21	26.4	1.622		2	0.34		2	21.39		2	21.73		2		58.18		2
2	2006	10	21	26.4	0.063		2	0.01		2	0.05		2	0.05		2		1.64		2
9	2006	10	21	26.4	1.619		2	0.34		2	21.38		2	21.72		2		58.15		2
Flag 2	accept	able	meas	urement	3: quest	ionable,	4: bad	5: below d	etction li	mit, 6: n	nean of rep	licate m	easurem	ent, 9: no	t reporte	q				Ĩ

Table AS	3. (Cor	tinue	(p													2006	<b>RMNS Int</b>	tercompari	ison Exe	rcise
LAB SAMP	LE YEAF	NOM S	DAY	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	XON	err	Flag	reduct	Silicate	err	Flag
39																				
-	2006	Ξ	10		0.54		2	0.63		2	4.48		2	5.11		2		25.67		2
2	2006	Ξ	10		2.97		2	0.18		2	25.08		2	25.26		2		139.32		2
3	2006	Ξ	10		3.39		2	0.09		2	35.02		2	35.11		2		106.48		2
4	2006	Ξ	10		1.80		2	0.36		2	8.79		2	9.15		2		49.53		2
5	2006	Ξ	10		0.15		2	0.08		2	0.11		2	0.18		2		1.78		2
9	2006	Ξ	10		2.00		2	0.38		2	9.23		2	9.61		2		34.93		2
40																				
-	2006	12	2	24	0.49	0.01	2			6			6			6				6
2	2006	12	2	24	2.55	0.02	2			6			6			6				6
3	2006	12	2	24	3.04	0.03	2			6			6			6				6
4	2006	12	7	24	1.60	0.01	2			6			6			6				6
2	2006	12	7	24	0.02	0.00	2			6			6			6				6
9	2006	12	2	24	1.61	0.01	2			6			6			6				6
42																				
-					0.46	0.004	2	0.67	0.004	2	5.62	0.038	2	6.29	0.041	2		27.11	0.191	2
2					2.54	0.013	2	0.084	0.002	2	34.13	0.413	2	34.22	0.413	2		150.6	0.174	2
3					3.078	0.025	2	0.017	0.001	2	43.5	0.091	2	43.6	0.09	2		134.6	1.26	2
4					1.62	0.005	2	0.353	0.001	2	22	0.118	2	22.3	0.041	2		59.45	0.187	2
5					0.024	0.015	2	0.015	0.002	2	0.02	0.046	2	0.034	0.048	2		1.99	0.042	2
9					1.626	0.007	2	0.356	0.002	2	21.8	0.37	2	22.15	0.37	2		59.42	0.071	2
43																				
-	2007	-	10		0.591	0.050	9	0.592	0:030	9	5.688	0.200	9	6.280	0.200	9		30.480	0.500	9
2	2007	-	10		2.887	0.050	9	0.071	0.030	9	34.338	0.200	9	34.410	0.200	9		152.862	0.500	9
3	2007	-	10		3.308	0.050	9	0.000	0:030	9	43.031	0.200	9	43.031	0.200	9		133.916	0.500	9
4	2007	-	10		1.740	0.050	9	0.307	0:030	9	22.359	0.200	9	22.666	0.200	9		59.207	0.500	9
5	2007	-	12		0.025	0.010	9	0.000	0.030	9	0.000	0.050	9	0.000	0.050	9		2.466	0.200	9
9	2007	-	10		1.726	0.050	9	0.325	0.030	9	22.049	0.200	9	22.374	0.200	9		58.475	0.500	9
44																				
-	2006	12	-		0.51	0.02	2	0.66	0.03	2	5.67	0.09	2			6		26.96	0.35	2
2	2006	12	-		2.55	0.08	2	0.17	0.02	2	33.16	0.19	2			6		152.21	0.18	2
3	2006	12	-		2.96	0.01	2	0.05	0.01	2	41.86	0.23	2			6		134.19	2.64	2
4	2006	12	-		1.56	0.02	2	0.39	0.02	2	21.55	0.15	2			6		59.25	1.58	2
5	2006	12	-		0.08	0.01	2	0.06	0.01	2	0.07	0.02	2			6		1.63	0.11	2
9	2006	12	-		1.60	0.06	2	0.39	0.02	2	20.99	0.19	2			6		58.64	0.35	2
Hag 2	accep	table n	neast	Irement	3: ques	tionable	e, 4: bad	. 5: below c	letction li	mit, 6: r	mean of rep	licate m	easurem	ent, 9: not	: reporte	g				

Table A	3. (Co	ntinu	ied)												2006	<b>RMNS Int</b>	tercompar	ison Ex	ercise
LAB SAM	PLE YEAF	NON F	DAY TEMP	Phospha	te err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	XON	err	Flag	reduct	Silicate	err	Flag
45																			ĺ
-	2006	10	31 22	0.54	0.06	2	0.67	0.09	2			6	6.5	0.85	2		30		2
2	2006	10	31 22	2.57		2	0.134	0.02	2			6	34		2		156		2
3	2006	10	31 22	3.00		2	<0.06		5			6	42		2		135		2
4	2006	10	31 22	1.62	0.18	2	0.35	0.05	2			6	21.8	2.83	2		60		2
5	2006	10	31 22	0.106	0.01	2	<0.06		5			6	<0.24		2		2.0	0.54	2
9	2006	10	31 22	1.61	0.18	2	0.37	0.05	2			6	21.7	2.82	2		60		2
46																			
-	2006	12	19 24.5	0.44	0.06	2	0.61	0.1	2	5.38	0.28	2	5.99	0.21	2		28.05	1.39	2
2	2006	12	19 24.5	2.48	0.12	2	0.10	0.1	2	32.26	0.49	2	32.36	0.49	2		149.97	6.96	2
3	2006	12	19 24.5	2.91	0.16	2	0.02	0.1	2	40.51	0.63	2	40.53	0.63	2		130.54	6.26	2
4	2006	12	19 24.5	1.54	0.09	2	0.33	0.1	2	20.47	0.42	2	20.80	0.35	2		55.56	2.78	2
5	2006	12	19 24.5	0.01	0.06	2	0.02	0.1	2	0.04	0.14	2	0.06	0.14	2		1.59	0.17	3
9	2006	12	19 24.5	1.56	0.09	2	0.35	0.1	2	20.54	0.42	2	20.89	0.35	2		56.08	2.78	2
47																			
-			16.5	0.810		2	0.604		2	5.687		2	6.292		2		28.937		2
2			16.5	4.394		2	0.088		2	34.191		2	34.297		2		157.938		2
3			16.5	4.481		2			5	43.275		2	43.275		2		135.913		2
4			16.5	2.274		2	0.332		2	21.925		2	22.257		2		58.532		2
2			16.5			5			5			5			5		1.428		2
9			16.5	2.271		2	0.336		2	22.070		2	22.406		2		57.956		2
48																			
-	2006	10	18 24.8	0.51	0.002	9			6			6	6.1	0.03	9		29.6	0.07	9
2	2006	10	18 24.8	2.51	0.005	9			6			6	33.4	0.03	9		155.3	0.07	9
3	2006	10	18 24.8	3.01	0.004	9			6			6	42.2	0.03	9		134.8	0.00	9
4	2006	10	18 24.8	1.61	0.002	9			6			6	21.8	0.03	9		58.5	0.07	9
5	2006	10	18 24.8	0.05	0.000	9			6			6	0.0	0.01	9		1.6	0.07	9
9	2006	10	18 24.8	1.61	0.000	9			6			6	21.7	0.10	9		58.5	0.00	9
49																			
-	2006	12	6 17	0.71	0.02	9	0.73	0.01	9			6	6.35	0.10	9	98	30.62	0.27	9
2	2006	12	6 17	2.63	0.02	9	0.20	0.01	9			6	33.99	0.29	9	98	163.99	0.42	9
3	2006	12	6 17	3.06	0.02	9	0.14	0.02	9			6	43.03	0.35	9	98	142.38	0.28	9
4	2006	12	6 17	1.78	0.02	9	0.48	0.01	9			6	22.14	0.19	9	98	60.40	0.57	9
5	2006	12	6 17	0.32	0.01	9	0.14	0.02	9			6	0.18	0.04	с	98	1.68	0.06	9
9	2006	12	6 17	1.77	0.01	9	0.49	0.01	9			6	22.10	0.22	9	98	60.06	0.32	9
Flag 2	accept	table r	neasuremer	it, 3: que	stionable	, 4: bad,	5: below c	etction li	imit, 6: r	mean of rep	dicate n	neasurem	ent, 9: no	t reporte	q				

Table AS	. (Con	tinue	(pe												2006 RMNS II	ntercompar	ison Exe	ercise
I A SAMF	LE YEAR	NON	DAY TEMP	Phospl	hate en	r Flag	Sitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag reduct	Silicate	err	Flag
50																		
-	2006	10	16 23.2	0.58	0.01	2	0.61	0.02	2	5.10	0.02	2	5.71	0.03	2	41.35	0.55	2
2	2006	10	16 23.2	0.38	0.01	2	0.17	0.01	2	29.93	0.44	2	30.10	0.44	2	212.27	2.25	з
3	2006	10	16 23.2	3.02	0.04	1	0.06	0.01	2	37.70	0.11	2	37.76	0.12	2	187.89	1.94	e
4	2006	10	16 23.2	1.40	0.02	2	0.32	0.02	2	20.06	0.16	2	20.38	0.17	2	81.6	0.48	2
5	2006	10	16 23.2	0.17	0.01	2	0.09	0.01	2	0.33	0.01	2	0.42	0.02	2			6
9	2006	10	16 23.2	1.42	0.01	2	0.16	0.01	2	10.06	0.07	2	10.22	0.07	2	174.65	1.36	3
51																		
-	2007	-	16 20.3	0.47		2	0.66		2	6.27		2			6	29.77		2
2	2007	-	16 20.3	2.58		2	0.13		2	34.24		2			6	153.99		2
e	2007	-	16 20.3	3.10		2	0.06		2	42.40		2			6	131.46		2
4	2007	-	16 20.3	1.62		2	0.41		2	20.94		2			6	60.76		2
2	2007	-	16 20.3	0.01		2	0.04		2	0.14		2			6	1.36		2
9	2007	-	16 20.3	1.65		2	0.43		2	21.23		2			6	61.06		2
52																		
-	2006	12 1	12	0.48	0.00	2	0.60	0.00	2	5.60	0.01	2			6	31.8	0.1	2
2	2006	12 1	12	2.43	0.01	2	0.08	00.00	2	33.0	0.1	2			6	168	0	2
3	2006	12 1	12	2.92	0.00	2	0.00	00.0	2	41.6	0.0	2			6	146	0	2
4	2006	12 1	12	1.55	0.00	2	0.33	0.00	2	21.3	0.0	2			6	63.2	0.2	2
5	2006	12	12	0.03	0.00	2	0.00	0.01	2	0.00	0.01	2			6	1.64	0.03	2
9	2006	12 1	12	1.55	0.01	2	0.33	0.00	2	21.3	0.0	2			6	63.0	0.1	2
53																		
-	2006	8	31	0.45		2	0.61		2	5.47		2	6.08		2	32.11		2
2	2006	8	31	2.42		2	0.10		2	34.14		2	34.24		2	158.36		2
3	2006	00	31	2.92		2	0.01		2	42.90		2	42.91		2	136.87		2
4	2006	00	31	1.56		2	0.34		2	21.27		2	21.61		2	56.62		2
5	2006	00	31	0.05		2	0.02		2	0.13		2	0.15		2	2.64		2
9	2006	8	31	1.53		2	0.35		2	21.13		2	21.48		2	58.18		2
54																		
5	2006	12 1	8	0.46		2	0.63		2	5.15		2	5.78		2	29.43		2
2	2006	12 1	8	2.49		2	0.10		2	33.58		2	33.68		2	157.73		2
3	2006	12 1	8	3.01		2	0.01		2	43.42		2	43.43		2	137.28		2
4	2006	12 1	8	1.60		2	0.34		2	21.06		2	21.40		2	59.41		2
5	2006	12 1	8	0.01		2	0.02		2	0.01		2	0.03		2	1.22		2
9	2006	12 1	18	1.60		2	0.35		2	21.02		2	21.37		2	59.26		2
Hag 2	accept	able n	neasureme	nt, 3: qu	lestiona	ble, 4: b	ad, 5: below	detction I	imit, 6: n	rean of rep	licate m	easureme	ent, 9: not	reporte	0			

Table A3	3. (Con	tinued)													2006	<b>RMNS Int</b>	ercompari	son Exe	rcise
LAB SAMPL	E YEAR	MON DA	TEMP	Phosphate	err	Flag	Nitrite	err	Flag	Nitrate	err	Flag	NOX	err	Flag	reduct	Silicate	err	Flag
55																			
-	2006	10 5	24.8	0.47	0.00	9	0.62	0.00	9	5.86	0.01	9	6.48	0.01	9	6.66	30.94	0.06	9
2	2006	10 5	24.8	2.51	0.00	9	0.09	0.00	9	34.18	0.07	9	34.26	0.07	9	6.66	158.25	0.26	9
з	2006	10 5	24.8	3.01	0.00	9	00.0	0.00	9	42.92	0.05	9	42.92	0.05	9	99.9	138.11	0.19	9
4	2006	10 5	24.8	1.59	0.00	9	0.34	0.00	9	22.16	0.03	9	22.50	0.03	9	99.9	60.99	0.05	9
5	2006	10 5	24.8	0.02	0.00	9	0.01	0.00	9	0.03	0.01	9	0.03	0.01	9	99.9	1.86	0.05	9
9	2006	10 5	24.8	1.60	0.00	9	0.34	0.00	9	22.19	0.02	9	22.53	0.02	9	99.9	61.03	0.09	9
56																			
-				0.5		2			6			6	6.40		2		29.67		2
2				2.51		2			6			6	33.80		2		155.92		2
3				3.03		2			6			6	40.81		2		135.79		2
4				1.6		2			6			6	21.77		2		58.87		2
5				0.05		2			6			6	0.01		2		1.7		2
9				1.55		2			6			6	22.0		2		58.57		2
Hag 2:	accept	able mea	surement	3: questi	onable,	4: bad,	5: below c	letction li	mit, 6: m	ean of rep	dicate m	easurem	ent, 9: not	reporte	q				

#### Appendix III

Scatter plots and histograms of the results



### Sample 1 Nitrate+Nitrite



Frequency distribution of nitrate+nitrite concentration of sample #1 ( lower panel)



#### Sample 2 Nitrate+Nitrite



Frequency distribution of nitrate+nitrite concentration of sample #2 ( lower panel)



### Sample 3 Nitrate+Nitrite



Frequency distribution of nitrate+nitrite concentration of sample #3 ( lower panel)



### Sample 4 Nitrate+Nitrite



Frequency distribution of nitrate+nitrite concentration of sample #4 ( lower panel)







Frequency distribution of nitrate+nitrite concentration of sample #5 ( lower panel)



### Sample 6 Nitrate+Nitrite



Frequency distribution of nitrate+nitrite concentration of sample #6 ( lower panel)



# Sample 1 Nitrate



Frequency distribution of nitrate concentration of sample #1 ( lower panel)



# Sample 2 Nitrate

Figure A2-2 Nitrate results: concentrations *versus* laboratory number ( upper panel)

Frequency distribution of nitrate concentration of sample #2 (lower panel)



# Sample 3 Nitrate



Frequency distribution of nitrate concentration of sample #3 (lower panel)



# Sample 4 Nitrate



Frequency distribution of nitrate concentration of sample #4 ( lower panel)



# Sample 5 Nitrate

Figure A2-5 Nitrate results: concentrations *versus* laboratory number ( upper panel)

Frequency distribution of nitrate concentration of sample #5 ( lower panel)



# Sample 6 Nitrate

Figure A2-6 Nitrate results: concentrations *versus* laboratory number ( upper panel)

Frequency distribution of nitrate concentration of sample #6 ( lower panel)



### Sample 1 Nitrite



Frequency distribution of nitrite concentration of sample #1 ( lower panel)



# Sample 2 Nitrite



Frequency distribution of nitrite concentration of sample #2 (lower panel)



# Sample 3 Nitrite



Frequency distribution of nitrite concentration of sample #3 (lower panel)



# Sample 4 Nitrite



Frequency distribution of nitrite concentration of sample #4 (lower panel)



# Sample 5 Nitrite



**F**requency distribution of nitrite concentration of sample #5 (lower panel)



# Sample 6 Nitrite



**Frequency distribution of nitrite concentration of sample #6 ( lower panel)** 



# Sample 1 Phosphate



Frequency distribution of phosphate concentration of sample #1 ( lower panel)



### Sample 2 Phosphate



Frequency distribution of phosphate concentration of sample #2 ( lower panel)



# Sample 3 Phosphate



Frequency distribution of phosphate concentration of sample #3 ( lower panel)



# Sample 4 Phosphate

 $\mu$  mol kg<sup>-1</sup> Figure A4-4 Phosphate results: concentrations *versus* laboratory number ( upper panel)

**Frequency distribution of phosphate concentration of sample #4 ( lower panel)** 



# Sample 5 Phosphate

 $\mu$  mol kg<sup>-1</sup> Figure A4-5 Phosphate results: concentrations *versus* laboratory number ( upper panel)

**Frequency distribution of phosphate concentration of sample #5 ( lower panel)** 



# Sample 6 Phosphate



**Frequency distribution of phosphate concentration of sample #6 ( lower panel)** 



# Sample 1 Silicate



Frequency distribution of silicate concentration of sample #1 ( lower panel)



# Sample 2 Silicate



Frequency distribution of silicate concentration of sample #2 (lower panel)



# Sample 3 Silicate



Frequency distribution of silicate concentration of sample #3 (lower panel)



# Sample 4 Silicate



Frequency distribution of silicate concentration of sample #4 (lower panel)



# Sample 5 Silicate

Figure A5-5 Silicate results: concentrations *versus* laboratory number ( upper panel)

Frequency distribution of silicate concentration of sample #5 ( lower panel)



# Sample 6 Silicate

**Figure A5-6 Silicate results: concentrations** *versus* **laboratory number ( upper panel)** 

Frequency distribution of silicate concentration of sample #6 (lower panel)

Apendix IV

Documents

IV – 1 Call for participating

7 June 2006

Dear Colleague,

This letter is to invite you to "Inter-comparison study for Reference Material of Nutrients in Seawater in a seawater matrix 2006".

The objective of this effort is to establish comparability on nutrient analyses in seawater among the laboratories/research vessles.

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

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

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

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

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

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

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

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

Best regards,

Michio AOYAMA, Dr. Senior Scientist Geochemical Res. Dep. Meteorological Research Institute e-mail: maoyama@mri-jma.go.jp Inter-comparison study for Reference Material of for Nutrients in Seawater in a seawater matrix 2006

#### **IMPORTANT DATES**

DEADLINE OF REPLY: 31 JULY 2006.

LIST OF PARTICIPANT: 15 AUGUST 2006.

SAMPLES SHIPPED BY : 15 SEPTEMBER 2006

**REPORTING DEADLINE: 25 DECEMBER 2006** 

EXPECTED DRAFT OF INTER-COMPARISON SUMARY: 28 FEBRUARY 2006

#### PLEASE RETURN THIS SHEET TO

kagaku22@mri-jma.go.jp

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

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

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

Name:

Affiliation:

Full postal address to receive samples

E-mail

Date:

Your comment:

Note: You can download this format from http://www.mri-jma.go.jp/Dep/ge/RMNScomp.html IV - 2 Instructions for RMNS bottles

#### Instructions for samples

1. Package contents

1) Your package contains 6 bottles

2) You will see the sample IDs, from sample1 to sample 6, and lab# with your name.

2. Preparations of samples

1) No preservatives have been added.

2) The details of preparation are given in a paper entitled "Reference material for nutrients in seawater in a seawater matrix".

#### 3. Analyses

1) Samples are ready for analyses, then please use them without filtration and just after you open the bottles. Again, no preservatives have been added, when opened their sterility will be lost.

2) Salinities of samples are as follows;

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

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

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

#### 4. Reporting of results

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

2) Please report one value for each parameter for each sample.

3) Participants are welcome to add your estimation on analytical uncertanity for each

parameter for each sample (ex.  $1.23\pm0.04$ ;  $23.45\pm0.67$ ).

4) REPORTING DEADLINE: 25 December 2006

Appendix V

History of nutrient inter-laboratory comparison study

#### Appendix VHistory of nutrient inter-laboratory comparison studies

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

#### **1. First ICES exercise**

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

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

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

#### 2. Second ICES exercise

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

#### <u>Part I</u>

The following research vessels participated:

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

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

#### <u>Part II</u>

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

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

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

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

#### 3. Third ICES exercise

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

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

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

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

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

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

#### 4. Fourth ICES exercise

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

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

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

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

#### 5. Fifth ICES exercise

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

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

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

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

#### 6. 2000 NOAA/NRC inter-comparison

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

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

#### 7. 2002 NOAA/NRC inter-comparison

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

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

Results for silicate, nitrite, and nitrate+nitrite in the distributed seawater samples were

acceptable for the majority of the participants and generally deviated by less than  $\pm 10\%$  from the assigned mean. All laboratories used methodologies based on colorimetric principles.

#### 8. 2003 MRI inter-comparison

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

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

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

#### 8. 2006 MRI inter-comparison

Autoclaved natural seawater was used for an inter-laboratory comparison study for a reference material for nutrients in seawater in 2006; this study was similar to the 2003 inter-laboratory comparison study. Sample homogeneity was confirmed by the repeatability of the measurements: for nitrate, phosphate and silicate, the homogeneities were 0.22%, 0.32% and 0.19%, respectively. Sets of six samples covered concentration ranges of 0.1–42.4  $\mu$ mol kg<sup>-1</sup> for nitrate, 0.0–0.6  $\mu$ mol kg<sup>-1</sup> for nitrite, 0.0–3.0  $\mu$ mol kg<sup>-1</sup> for phosphate, and 1.7–156.1  $\mu$ mol kg<sup>-1</sup> 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.