

2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater

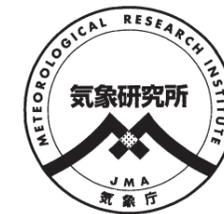
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気象研究所技術報告

第 60 号

栄養塩測定用海水組成標準の 2008 年国際共同実験報告



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Preface

Nutrients and total inorganic carbon have been the major observational variables in various international global ocean observation expeditions, such as the Geochemical Ocean Sections Study (GEOSECS) in the 1970s, the World Ocean Circulation Experiment (WOCE) in the 1990s, and the ongoing Climate Variability and Predictability (CLIVAR). Observation of the natural variability of nutrients and inorganic carbon in the world's oceans, and investigation of temporal and spatial changes due to the oceans' response to climate change and increasing carbon dioxide in the atmosphere, continue to be important topics of oceanographic research. Therefore, the comparability and traceability of nutrient data in the world's oceans are fundamental issues in marine science, particularly for studies of global climate change. The oceanographic community has continued to improve comparability of nutrient data from the world's oceans in many ways, including through international inter-comparison exercises and the development of nutrient reference materials.

However, as reported in "Climate Change 2007 – The Physical Science Basis" (Intergovernmental Panel on Climate Change [IPCC], Bindoff, et al., 2007), adequate comparability and traceability of nutrient data have not yet been achieved. IPCC 2007 (Bindoff et al., 2007) includes the following comments regarding nutrient comparability:

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

Current knowledge about the variability of nutrient concentrations in seawater is limited because of the lack of a sufficient technique to determine small variations in nutrients. Therefore we need an adequate nutrient scale system to establish the traceability and comparability of nutrient data in addition to data with high accuracy and

high precision.

The Geochemical Research Department of the Meteorological Research Institute (MRI) of Japan began developing seawater-based reference materials for nutrient analysis about 10 years ago. This research continues today as part of the study entitled “An observational study on variation mechanism of carbon cycle in the ocean.” One of the major goals of this research is the development of standard materials for the analysis of nutrients in seawater that satisfy the requirements for oceanographic research. In February 2009, the MRI and several national and international institutes and organizations sponsored a 2009 International Nutrients Scale System (INSS) workshop in Paris, organized by an MRI scientist (M. Aoyama) and his collaborators. This workshop focused on the ongoing international collaboration with the aim of establishing global comparability of nutrient data from the world's oceans. Participants of the workshop agreed that by establishing the INSS, the comparability and traceability of nutrient data in seawater could be ensured. Thus, not only will the study of nutrients in seawater move forward, but also the amount of accumulated anthropogenic CO₂ in the ocean will be accurately evaluated, as both are essential for the study of global warming. The workshop also sent a proposal to the 25th Intergovernmental Oceanographic Commission (IOC) general assembly entitled “ICES-IOC Study Group on Nutrients Standards - SGONS,” and the proposal was adopted by the general assembly in June 2009.

We are now progressing toward having seawater-based nutrient reference materials with stability and homogeneity that are sufficient to satisfy our present requirements. To establish an International Nutrients Scale System and global standard material for nutrient analysis in seawater, a worldwide, inter-laboratory comparison study is an important step. This technical report summarizes results of the third inter-calibration exercise conducted by MRI in 2008, in which 56 laboratories participated.

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序文

栄養塩及び無機炭素は、1970年代におけるGEOSECSや1990年代のWOCE、及び現在実施中のCLIVARなど様々な国際的海洋計測プロジェクトにおいて重要な測定項目として取り上げられてきた。世界の海洋における栄養塩と無機炭素の自然変動観測及び、気候変動や大気中の二酸化炭素の増大に呼応して引き起こされる経時的／空間的変動の究明は、海洋研究における重要課題であり続ける。それゆえ、世界の海洋における栄養塩データの比較及びトレーサビリティは海洋科学、特に世界的変動の究明において基本的課題のひとつである。

しかし、「気候変動2007」－The Physical Science Basis (Bindoff et al., 2007)に報告されるように、十分な比較及びトレーサビリティは未だ達成されていない。

「気候変動2007」(Bindoff et al., 2007)では栄養塩の比較可能性（コンパラビリティ）は次のように報告されている。「世界に配布された同じデータセットを使って、地域によって栄養塩比率の大きな変動が検出されたものの、一貫した海盆規模傾向は見られなかった。深海における栄養塩の計測の不確かさは、栄養塩変動におけるコヒーレンスの欠如によるものとも考えられる。不正確さの原因として、観測数は限られることや、異なる時期におけるラボ間の比較可能性（コンパラビリティ）の欠如などがあげられる。」

最近まで海水中の栄養塩の分析では、提案された基準（特に、確度）を満足することができていない。その主要な原因は、海水中の栄養塩の分析に関して、基準を満足させるための標準物質ないし参照物質が提供されなかったためである。そのため、現在に至るも海洋における栄養塩の変動に関する知識も限られている。従って、変動を検出するためには、高精度であるばかりでなく比較可能性（コンパラビリティ）やトレーサビリティのある栄養塩データを得るために必要な標準物質ないし参照物質の確立が求められている。

1990年代の中頃より、気象研究所地球化学研究部では、海水をベースにした

栄養塩の参照物質を作成する研究を始めた。この研究は今日“海洋中炭素循環変動の実態把握とメカニズム解明に関する研究”のサブ課題1“長期変化傾向を検出するための観測・品質管理手法の開発”の一部として研究が進められている。主な目標は、海水中の栄養塩分析に関して海洋学的要求を満たした国際的な栄養塩測定標準システムを構築することである。2009年2月には、気象研究所と世界の研究所及び国際組織が合同で、パリで開催された2009 INSS（国際栄養塩スケールシステム）ワークショップを後援した。このワークショップは気象研究所の研究者が中心となって組織したものである。このワークショップでは、世界の海洋の栄養塩データの比較可能性の確立を目的として、現在進行中でもある世界的な協力体制に焦点が当てられた。海水の比較可能性及びトレサビリティを確立するためのINSS（国際栄養塩スケールシステム）を構築することで参加者の同意が得られた。つまり、栄養塩の研究が前進するだけでなく、海洋に蓄積した人為起源二酸化炭素の量が精確に検出できるということであり、これら両方が地球温暖化の研究に必須とされる。また、2009年6月に開催された第25回IOC総会にむけて、栄養塩標準のICES-IOC研究グループSGONS（A JOINT ICES-IOC STUDY GROUP ON NUTRIENT STANDARDS）の提案がなされ採択されている。

現在、栄養塩標準物質のシステム構築の過程で、必要な一歩として、栄養塩標準の国際的な共同実験がある。この技術報告では、2008年に56機関の参加で行なわれた第3回国際共同実験の結果が取りまとめられている。

地球化学研究部第2研究室長 緑川 貴

Abstract

Autoclaved natural seawater collected in the North Pacific Ocean was used as a reference material for nutrients in seawater (RMNS) during an inter-laboratory comparison (I/C) study conducted in 2008. This study was a follow-up to previous studies conducted in 2003 and 2006. A set of six samples was distributed to each of 58 laboratories in 15 countries around the globe, and results were returned by 54 of those laboratories (15 countries). The homogeneities of samples used in the 2008 I/C study, based on analyses for three determinants, were improved compared to those of samples used in the 2003 and 2006 I/C studies.

Results of these I/C studies indicate that most of the participating laboratories have an analytical technique for nutrients that is sufficient to provide data of high comparability. The differences between reported concentrations from the same laboratories in the 2006 and 2008 I/C studies for the same batch of RMNS indicate that most of the laboratories have been maintaining internal comparability for two years. Thus, with the current high level of performance in the participating laboratories, the use of a common reference material and the adaptation of an internationally accepted nutrient scale system would increase comparability among laboratories worldwide, and the use of a certified reference material would establish traceability.

In the 2008 I/C study we observed a problem of non-linearity of the instruments of the participating laboratories similar to that observed among the laboratories in the 2006 I/C study. This problem of non-linearity should be investigated and discussed to improve comparability for the full range of nutrient concentrations. For silicate comparability in particular, we see relatively larger consensus standard deviations than those for nitrate and phosphate.

要旨

栄養塩測定用海水組成標準の2008年国際共同実験が行われた、この国際共同実験では、オートクレーブで滅菌処理された天然海水が試料として用いられた。この国際共同実験は、2003年および2006年に行なわれた国際共同実験に引き続き実施された。2008年国際共同実験で使用された試料の均一性は、2003年および2006年共同実験で使われたものより向上している。15カ国58機関に試料が送付され、15カ国54機関から結果が報告された。

この共同実験の結果は、参加した機関のほとんどのところは優れたコンパラビリティ（比較可能性）を確保するにたる十分な分析能力を持っていることを示している。2006年共同実験および2008年共同実験の双方で配布された同一の栄養塩標準の分析結果は、多くの機関が2年間にわたる機関内のコンパラビリティ（比較可能性）を維持していることを示している。従って、現在の高い水準の分析能力を基礎として、共通の標準物質の使用と国際栄養塩スケールの承認は異なる機関間の栄養塩データの追跡可能性（トレーサビリティ）を向上させるとともに、認証標準物質の使用が全海洋での栄養塩データの追跡可能性（トレーサビリティ）を確立させるであろう。

しかし我々は2006年共同実験の時と同様に、各機関の分析時における検量線の非直線性の扱い方の違いが各機関相互の栄養塩濃度の報告値の違いの主たる原因の一つであることを見出した。この非直線性の扱い方を議論し調査することは海洋での全濃度レンジにおけるコンパラビリティ（比較可能性）を確保するうえで必要である。ケイ酸塩のコンパラビリティ（比較可能性）に関しては、我々は硝酸塩やリン酸塩に比べて大きな標準偏差を見出した。

Contents

1. Introduction	1
2. Samples.....	3
2.1 Sample preparation and timetable for the inter-laboratory comparison study.....	3
2.2 Selection of determinants.....	3
2.3 Sample homogeneity.....	3
3. Participants and response	5
4. Statistical treatment	7
4.1 Raw mean, median, and standard deviation	7
4.2 Robust statistics	7
4.3 Consensus mean, median, and standard deviation.....	7
4.4 Calculation of Z-scores	7
5. Results	11
5.1 Ranked scatter-plots of the results	11
5.2 Consensus means, medians, and standard deviations	17
5.3 Comparison between consensus standard deviation and homogeneity of Sample3	19
5.4 Summary of analytical precision of participating laboratories and consensus standard deviation.....	19
5.5 Z-scores.....	21
6. Comparability between results from 2006 and 2008 RMNS I/C studies	36
7. Discussion and conclusions	45
Acknowledgements	45
References	46
Appendix I Participating Laboratories	49
Appendix II Results reported by participants	59
Appendix III Scatter plots and histograms of the results from participating laboratories	83
Appendix IV Documents related to 2008 inter-comparison study	115
IV-1 Call for participating.....	117
IV-2 Instructions for samples.....	121
IV-3 Follow-up survey for silicate standards.....	123
Appendix V	127

List of Tables and Figures

Tables

Table 1. Homogeneity of samples with the highest nutrient concentrations in I/C studies in 2003, 2006, and 2008, and the analytical precision of 30 seawater replicate analyses in 2008.....	4
Table 2. Summary of responses from participants.....	5
Table 3. Raw and robust statistics for nutrient concentrations calculated using all reported values.....	9
Table 4. Consensus means, medians, and standard deviations for the 7 samples.....	17
Table 5. Comparison between homogeneity and consensus coefficient of variation of nutrient measurements in Sample3.....	19
Table 6-1. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample1.....	19
Table 6-2. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample2.....	20
Table 6-3. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample3.....	20
Table 6-4. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample4.....	20
Table 6-5. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample5.....	21
Table 6-6. Median and range of analytical precision of participating laboratories, and consensus coefficient of variation for analyses of nutrients in Sample6.....	21
Table 7-1. Z-scores for nitrate+nitrite analyses.....	22
Table 7-2. Z-scores for nitrate analyses.....	24
Table 7-3. Z-scores for nitrite analyses.....	26
Table 7-4. Z-scores for phosphate analyses.....	28
Table 7-5. Z-scores for silicate analyses.....	30
Table 7-6. Combined Z-scores for phosphate and nitrate+nitrite analyses.....	32
Table 7-7. Combined Z-scores for phosphate, nitrate+nitrite, and silicate analyses.....	34
Table 8-1. Comparison between nitrate+nitrite results from 2006 and 2008 RMNS I/C studies.....	37
Table 8-2. Comparison between nitrate results from 2006 and 2008 RMNS I/C studies.....	38
Table 8-3. Comparison between nitrite results from 2006 and 2008 RMNS I/C studies.....	39
Table 8-4. Comparison between phosphate results from 2006 and 2008 RMNS	

I/C studies.....	40
Table 8-5. Comparison between silicate results from 2006 and 2008 RMNS I/C studies.....	41
Table A1. List of participants.....	51
Table A2. Cross reference for Lab numbers in 2008, 2006, and 2003 I/C studies.....	55
Table A3. Nutrient results reported by the participants.....	61
Table A4. Ammonia results reported by the participants. All concentrations are $\mu\text{mol kg}^{-1}$	76
Table A5. Dissolved organic phosphate (DOP) results reported by the participants. Concentrations are in $\mu\text{mol kg}^{-1}$	79
Table A6. Dissolved organic nitrogen (DON) results reported by the participants. All concentrations are in $\mu\text{mol kg}^{-1}$	80
Table A7. Dissolved organic carbon (DOC) results reported by the participants. All concentrations are in $\mu\text{mol kg}^{-1}$	81

Figures

Figure 1. Nitrate+Nitrite results for all samples. Laboratories are ranked in order of concentrations reported for Sample3.....	12
Figure 2. Nitrate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3.....	13
Figure 3. Nitrite results for all samples. Laboratories are ranked in order of concentrations reported for Sample6.....	14
Figure 4. Phosphate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3.....	15
Figure 5. Silicate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3.....	16
Figure 6. Cumulative distribution of reported nitrate concentrations in 2006 and 2008 I/C studies.....	42
Figure 7. Comparability of nitrate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.....	42
Figure 8. Cumulative distribution of reported phosphate concentrations in 2006 and 2008 I/C studies.....	43
Figure 9. Comparability of phosphate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.....	43
Figure 10. Cumulative distribution of reported silicate concentrations in 2006 and 2008 I/C studies.....	44
Figure 11. Comparability of silicate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.....	44
Figure A1-1 Nitrate+nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #1 (lower panel).....	85
Figure A1-2 Nitrate+nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #2 (lower panel).....	86
Figure A1-3 Nitrate+nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #3 (lower panel).....	87
Figure A1-4 Nitrate+nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #4 (lower panel).....	88
Figure A1-5 Nitrate+nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #5 (lower panel).....	89
Figure A1-6 Nitrate+nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #6 (lower panel).....	90
Figure A2-1 Nitrate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #1 (lower panel).....	91

Figure A2-2 Nitrate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #2 (lower panel).....	92
Figure A2-3 Nitrate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #3 (lower panel).....	93
Figure A2-4 Nitrate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #4 (lower panel).....	94
Figure A2-5 Nitrate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #5 (lower panel).....	95
Figure A2-6 Nitrate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #6 (lower panel).....	96
Figure A3-1 Nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #1 (lower panel).....	97
Figure A3-2 Nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #2 (lower panel).....	98
Figure A3-3 Nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #3 (lower panel).....	99
Figure A3-4 Nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #4 (lower panel).....	100
Figure A3-5 Nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #5 (lower panel).....	101
Figure A3-6 Nitrite: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #6 (lower panel).....	102
Figure A4-1 Phosphate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #1 (lower panel)	103
Figure A4-2 Phosphate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #2 (lower panel)	104
Figure A4-3 Phosphate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #3 (lower panel)	105
Figure A4-4 Phosphate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #4 (lower panel)	106
Figure A4-5 Phosphate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported phosphate concentration for	

sample #5 (lower panel)	107
Figure A4-6 Phosphate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #6 (lower panel)	108
Figure A5-1 Silicate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #1 (lower panel).....	109
Figure A5-2 Silicate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #2 (lower panel).....	110
Figure A5-3 Silicate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported silicate concentration of sample #3 (lower panel).....	111
Figure A5-4 Silicate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported silicate concentration of sample #4 (lower panel).....	112
Figure A5-5 Silicate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #5 (lower panel).....	113
Figure A5-6 Silicate: concentrations <i>versus</i> laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #6 (lower panel)	114