

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

BY

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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



気象研究所

METEOROLOGICAL RESEARCH INSTITUTE, JAPAN

January 2010

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気 象 研 究 所 技 術 報 告 ISSN 0386-4049  
第 60 号

平成 22 年 3 月 発 行

編 集 兼  
発 行 者

気 象 研 究 所

〒305-0052 茨城県つくば市長峰1-1  
TEL(029)853-8535

印 刷 者

松枝印刷株式会社  
〒303-0034 茨城県常総市水海道天満町 2438

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Michio Aoyama<sup>1\*</sup>, Carol Anstey<sup>2</sup>, Janet Barwell-Clarke<sup>3</sup>, François Baurand<sup>4</sup>, Susan Becker<sup>5</sup>, Marguerite Blum<sup>6</sup>, Stephen C. Coverly<sup>7</sup>, Edward Czobik<sup>8</sup>, Florence d'Amico<sup>9</sup>, Ingela Dahllöf<sup>10</sup>, Minhan Dai<sup>11</sup>, Judy Dobson<sup>12</sup>, Olivier Pierre-Duplessix<sup>13</sup>, Magali Duval<sup>14</sup>, Clemens Engelke<sup>12</sup>, Gwo-Ching Gong<sup>15</sup>, Olivier Grosso<sup>16</sup>, Atsushi Hirayama<sup>17</sup>, Hiroyuki Inoue<sup>18</sup>, Yuzo Ishida<sup>19</sup>, David J. Hydes<sup>20</sup>, Hiromi Kasai<sup>21</sup>, Roger Kerouel<sup>22</sup>, Marc Knockaert<sup>23</sup>, Nurit Kress<sup>24</sup>, Katherine A. Kroglund<sup>25</sup>, Masamitsu Kumagai<sup>26</sup>, Sophie C. Leterme<sup>27</sup>, Claire Mahaffey<sup>28</sup>, Hitoshi Mitsuda<sup>29</sup>, Pascal Morin<sup>30</sup>, Thierry Moutin<sup>16</sup>, Dominique Munaron<sup>31</sup>, Akihiko Murata<sup>32</sup>, Günther Nausch<sup>33</sup>, Hiroshi Ogawa<sup>34</sup>, Jan van Ooijen<sup>35</sup>, Jianming Pan<sup>36</sup>, Georges Paradis<sup>37</sup>, Chris Payne<sup>38</sup>, Gary Prove<sup>39</sup>, Patrick Raimbault<sup>40</sup>, Malcolm Rose<sup>41</sup>, Kazuhiro Saito<sup>42</sup>, Hiroaki Saito<sup>43</sup>, Kenichiro Sato<sup>44</sup>, Cristopher Schmidt<sup>45</sup>, Monika Schütt<sup>46</sup>, Theresa M. Shammon<sup>47</sup>, Solveig Olafsdottir<sup>48</sup>, Jun Sun<sup>49</sup>, Toste Tanhua<sup>50</sup>, Sieglinde Weigelt-Krenz<sup>51</sup>, Linda White<sup>52</sup>, E. Malcolm S. Woodward<sup>53</sup>, Paul Worsfold<sup>54</sup>, Takeshi Yoshimura<sup>55</sup>, Agnès Youénoù<sup>22</sup>, Jia-Zhong Zhang<sup>56</sup>

- 1) Geochemical Research Department, Meteorological Research Institute, Tsukuba, Japan
- 2) Department of Fisheries and Oceans, Bedford Institute of Oceanography, Nova Scotia, Canada
- 3) Department of Fisheries and Oceans Canada, Institute of Ocean Sciences, Sidney, British Columbia, Canada
- 4) Institut de Recherché pour le Développement, Campus Ifremer Technopole de Brest-Iroise, Plouzane, France
- 5) Scripps Institution of Oceanography, University of California, San Diego, California, USA
- 6) Monterey Bay Aquarium Research Institute, California, USA
- 7) SEAL Analytical GmbH, Norderstedt, Germany
- 8) NSW Department of Environment and Climate Change, New South Wales Government, Lidcombe, New South Wales, Australia
- 9) Station d'Arcachon, Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER), Arcachon, France
- 10) Department of Marine Ecology, National Environmental Research Institute, Aarhus University, Roskilde, Denmark
- 11) State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China
- 12) Scottish Environment Protection Agency, Marine Chemistry, Scotland, United Kingdom
- 13) Laboratoire Environment Ressources de Normandie (LERN), Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER), Port en Bessin,

- France
- 14) Laboratoire Environnement-Ressources d'Aquitaine (LER-AR), Institut Français de Recherche Pour l'Exploitation de la Mer (IFREMER), Arcachon, France
  - 15) Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University, Keelung, Taiwan
  - 16) Laboratoire d'Océanographie Physique et Biogéochimique, Marseille, France
  - 17) Oceanographical Division, Maizuru Marine Observatory, Maizuru, Japan
  - 18) Oceanographic Division, Nagasaki Marine Observatory, Nagasaki, Japan
  - 19) Global Environment and Marine Department, Japan Meteorological Agency, Tokyo, Japan
  - 20) National Oceanography Centre, Southampton, United Kingdom
  - 21) Hokkaido National Fisheries Research Institute, Fisheries Research Agency, Hokkaido, Japan
  - 22) Department of DYNECO/Pelagos, Institut Français de Recherche pour l'Exploitation de la Mer (IFREMER), Brest, France
  - 23) Department of MARCHEM, Management of Unit of the North Sea Mathematical Models, Royal Belgian Institute of Natural Sciences (MUMM), Oostende, Belgium
  - 24) National Institute of Oceanography, Israel Oceanographic and Limnological Research, Haifa, Israel
  - 25) School of Oceanography, University of Washington, Seattle, Washington, USA
  - 26) Marine Division, Hakodate Marine Observatory, Hakodate, Japan
  - 27) School of Biology, Flinders University, Adelaide, Australia
  - 28) Department of Earth and Ocean Science, University of Liverpool, Liverpool, United Kingdom
  - 29) Laboratory for Instrumentation and Analysis, The General Environmental Technos Co., Ltd. (KANSO TECHNOS), Osaka, Japan
  - 30) Marine Chemistry Laboratory, French National Center for Scientific Research (CNRS) and University Pierre et Marie Curie Paris VI and University Bretagne Occidentale, Roscoff, France
  - 31) Laboratoire Environnement Ressources, Institut Français de Recherche pour l'Exploitation de la Mer (IFREMER), Sète, France
  - 32) Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Yokosuka, Japan
  - 33) Department of Marine Chemistry, Leibniz Institute for Baltic Sea Research, Rostock-Warnemünde, Germany
  - 34) Ocean Research Institute, University of Tokyo, Tokyo, Japan
  - 35) Royal Netherlands Institute for Sea Research (NIOZ), Texel, the Netherlands
  - 36) The Second Institute of Oceanography, State Oceanic Administration, Hangzhou, China
  - 37) Marine Science Institute, University of California Santa Barbara, Santa Barbara, California, USA
  - 38) Earth and Ocean Sciences Department, University of British Columbia, Vancouver, British Columbia, Canada
  - 39) Environmental Waters Laboratory, Queensland Health Forensic and Scientific Services, Coopers Plains, Australia

- 40) Centre d'Océanologie de Marseille - Service d'Observation, Marseille, France
- 41) Marine Laboratory, Fisheries Research Services, Aberdeen, United Kingdom
- 42) Oceanographical Division, Kobe Marine Observatory, Kobe, Japan
- 43) Biological Oceanography, Tohoku National Fisheries Research Institute, Fisheries Research Agency, Miyagi, Japan
- 44) Marine Works Japan Ltd. (MWJ), Yokohama, Japan
- 45) Geochemical and Environmental Research Group, Texas A&M University, Texas, TX, USA
- 46) Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Hamburg, Germany
- 47) Department of Local Government and the Environment, Isle of Man Government Laboratory, Douglas, Isle of Man, British Isles
- 48) Marine Research Institute, Reykjavik, Iceland
- 49) Key Laboratory of Marine Ecology & Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China
- 50) Leibniz Institute of Marine Sciences, IFM-GEOMAR, Kiel, Germany
- 51) BSH Bundesamt für Seeschifffahrt und Hydrographie (Federal Maritime and Hydrographic Agency), Hamburg, Germany
- 52) Ocean Science Division, Institute of Ocean Sciences, Sidney, British Columbia, Canada
- 53) Plymouth Marine Laboratory, Plymouth, United Kingdom
- 54) School of Earth, Ocean & Environmental Sciences, University of Plymouth, Plymouth, United Kingdom
- 55) Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, Abiko, Japan
- 56) Ocean Chemistry Division, Atlantic Oceanographic and Meteorological Laboratory (AOML), National Oceanic and Atmospheric Administration, Miami, Florida, USA

\*Coordinator, 2008 inter-laboratory comparison study





## 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 CO<sub>2</sub> 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.

Takashi Midorikawa  
Head of the Second Research Laboratory  
Geochemical Research Department  
Meteorological Research Institute

## 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。

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## 1. Introduction

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

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

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

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

In 2003 and 2006, the Meteorological Research Institute of Japan (MRI) conducted I/C studies with two main differences from previous studies. First, the nutrient concentrations in the distributed samples were set to cover the concentration range of nutrients in the Pacific Ocean, which has the highest nutrient concentrations among the open oceans of the world. Second, the distributed samples were prepared in a natural seawater matrix in a single bottle so that four determinants (nitrate, nitrite, phosphate, and silicate) could be simultaneously analyzed.

In the 2003 I/C study, the consensus standard deviations were 4.5 times the homogeneities for phosphate and more than 10 times those of silicate. For nitrate, the standard deviations were only about double the homogeneities. These results indicated

that the variability between “in-house” standards in the participating laboratories, rather than analytical precision, was the primary source of inter-laboratory differences.

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

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

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

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

## 2. Samples

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

Natural seawater was collected in the North Pacific Ocean and depth of surface, and nutrient concentration maximum depth around 1500m. Seawater was placed into a 230-L stainless steel container and autoclaved twice at 120 °C for 2 h. Aliquots of 90 mL of the autoclaved seawater were then transferred into polypropylene bottles. This procedure for preparing samples was based on a previously reported method for preparing a reference material for the determination of nutrients in seawater (Aminot and Kerouel, 1991, 1995). The sample homogeneity was confirmed by repeatability of analytical measurements. Long-term storage of our RMNS samples for up to 4 years at room temperature has shown that the homogeneities and concentrations of nutrients are maintained for about at least this length of time (Aoyama *et al.*, 2007).

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

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

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

### 2.2 Selection of determinants

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

### 2.3 Sample homogeneity

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

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

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

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

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

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



### 3. Participants and response

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

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

**Table 2. Summary of responses from participants.**

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

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

Nutrient	Sample #	Number of results		Nutrient	Sample #	Number of results	
		Received	Statistically treated			Received	Statistically treated
Ammonia	1	12		Dissolved	1	1	
	2	14		organic	2	5	
	3	14		nitrogen	3	5	
	4	14		(DON)	4	5	
	5	12			5	1	
	6	12			6	1	
	7	2			7	1	
	8	8			8	1	
Dissolved organic phosphate (DOP)	1	2		Dissolved	1	1	
	2	5		organic	2	1	
	3	5		carbon	3	1	
	4	5		(DOC)	4	1	
	5	2			5	1	
	6	3			6	1	
	7	1			7	0	
	8	1			8	0	

## 4. Statistical treatment

### 4.1 Raw mean, median, and standard deviation

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

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

### 4.2 Robust statistics

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

### 4.3 Consensus mean, median, and standard deviation

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

### 4.4 Calculation of Z-scores

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

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

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

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

7-5.

Combined  $Z$ -scores were also calculated for  $Z_{\text{NO}_x} + Z_p$  and  $Z_{\text{NO}_x} + Z_p + Z_s$  for each sample at each laboratory and are shown in Tables 7-6 and 7-7, where  $Z_{\text{NO}_x}$ ,  $Z_p$ , and  $Z_s$  are the  $Z$ -scores for nitrate+nitrite, phosphate and silicate, respectively. If concentrations of nitrate+nitrite were not reported, nitrate was used instead.

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

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

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

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

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

## 5. Results

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

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

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

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

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

### 5.1 Ranked scatter-plots of the results

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

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

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

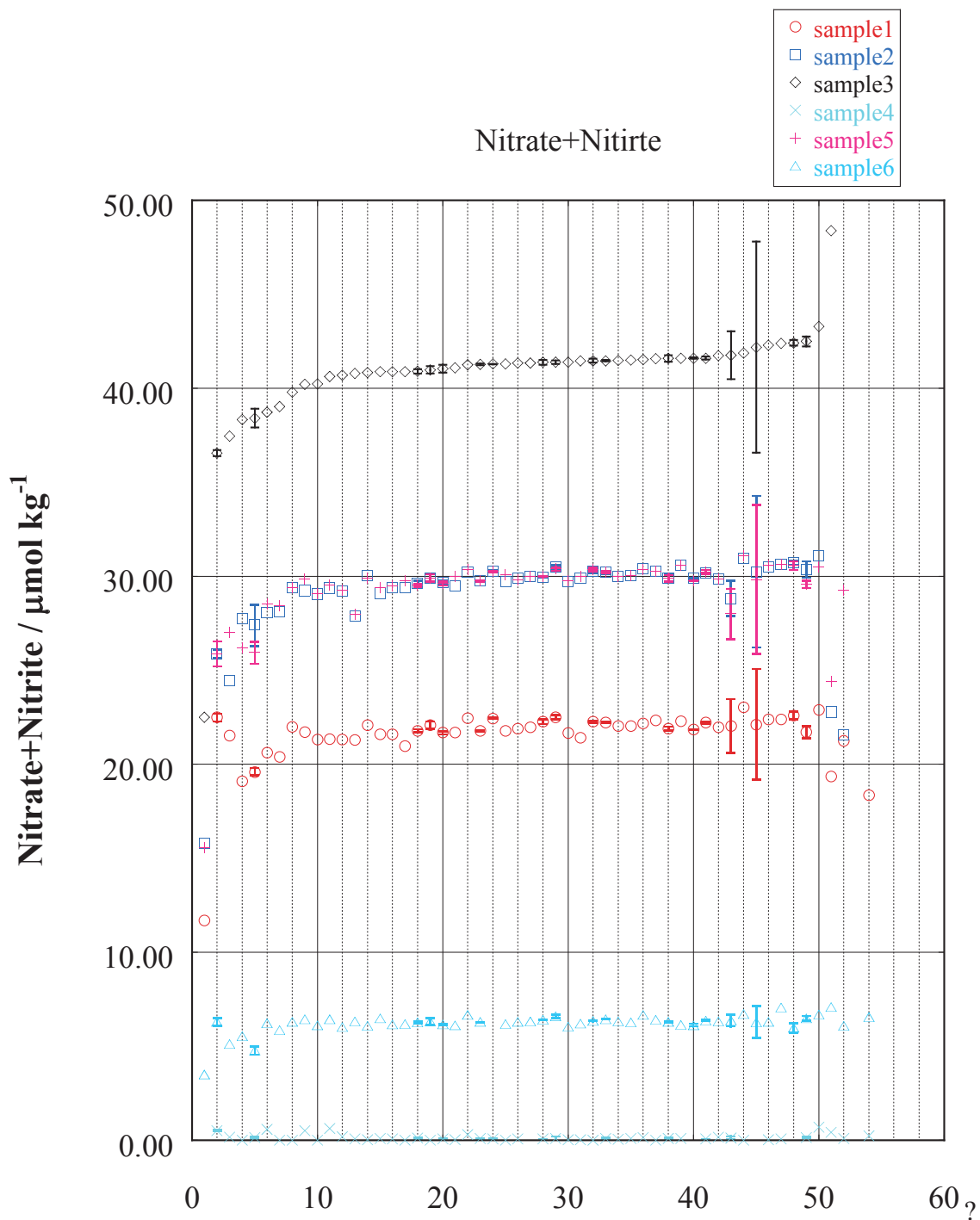


Figure 1. Nitrate+Nitrite results for all samples. Laboratories are ranked in order of concentrations reported for Sample3.



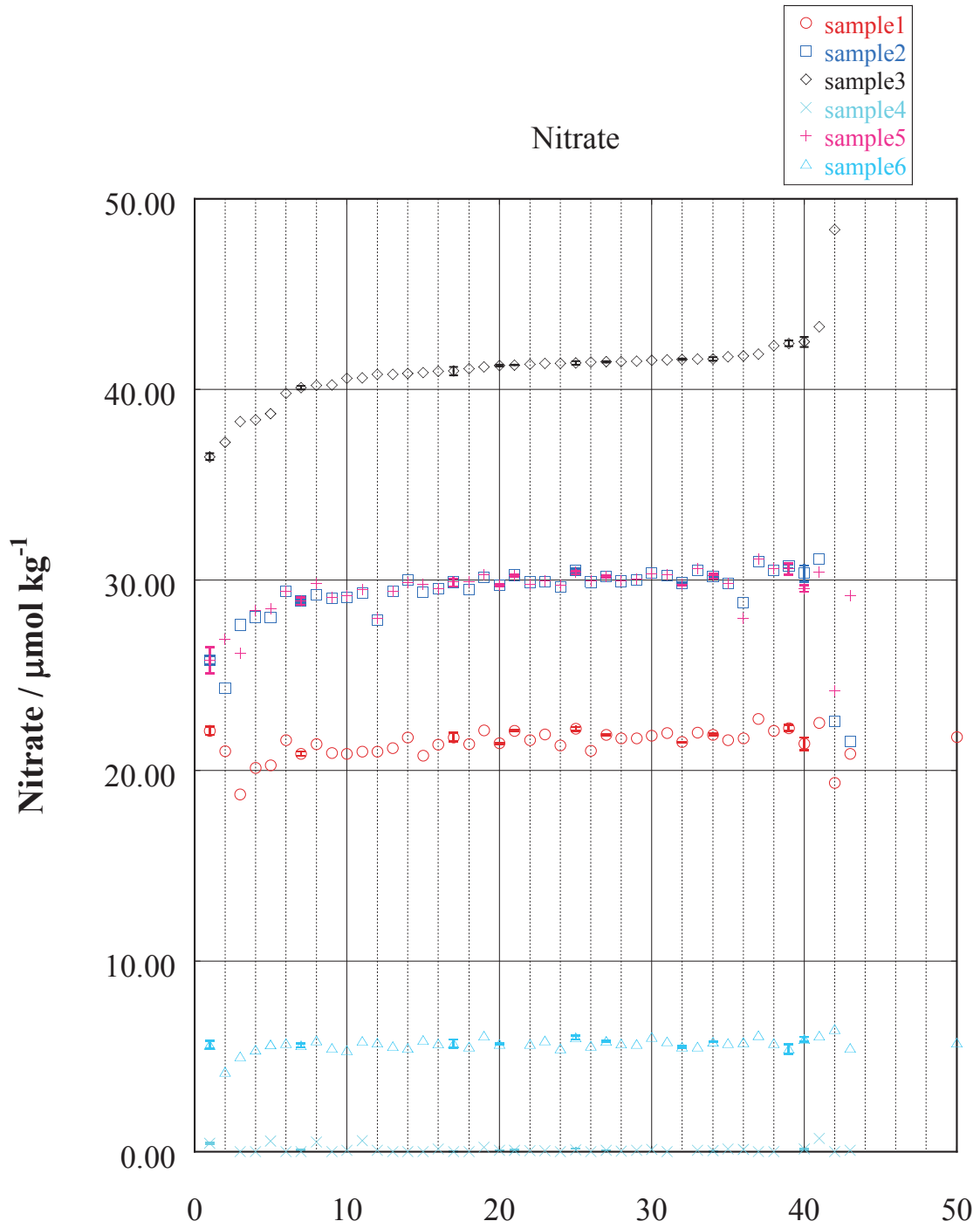


Figure 2. Nitrate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3

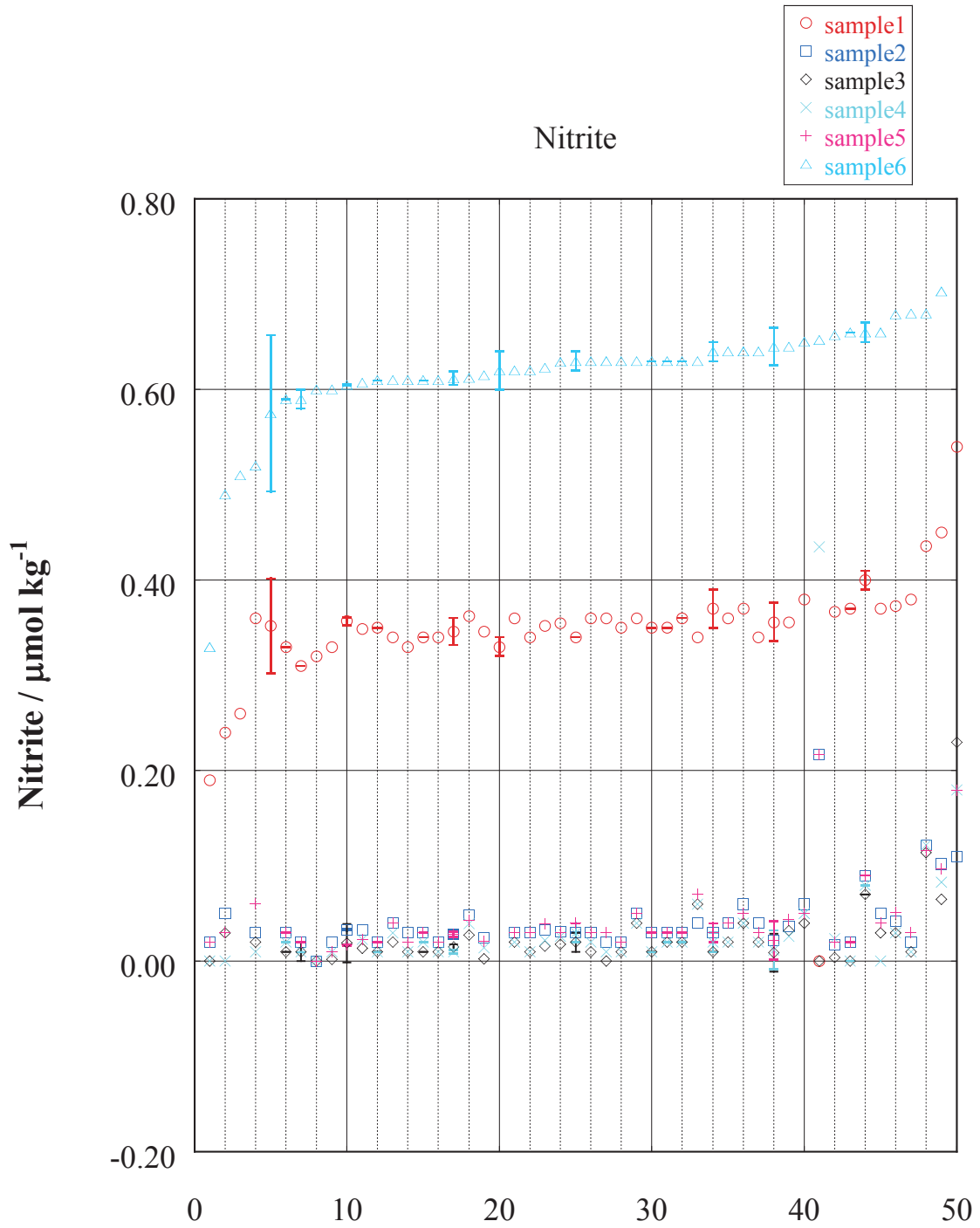


Figure 3. Nitrite results for all samples. Laboratories are ranked in order of concentrations reported for Sample6

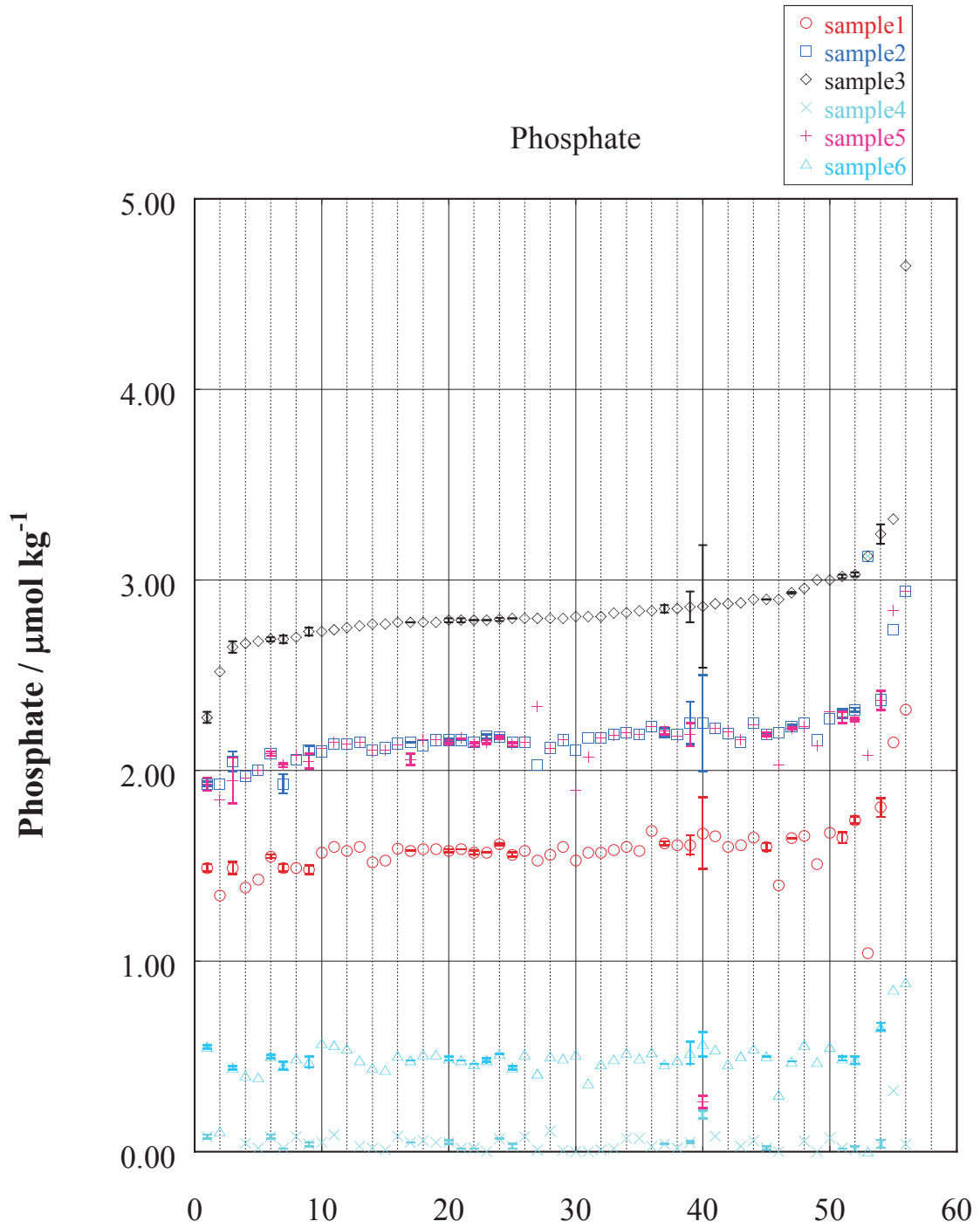


Figure 4. Phosphate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3

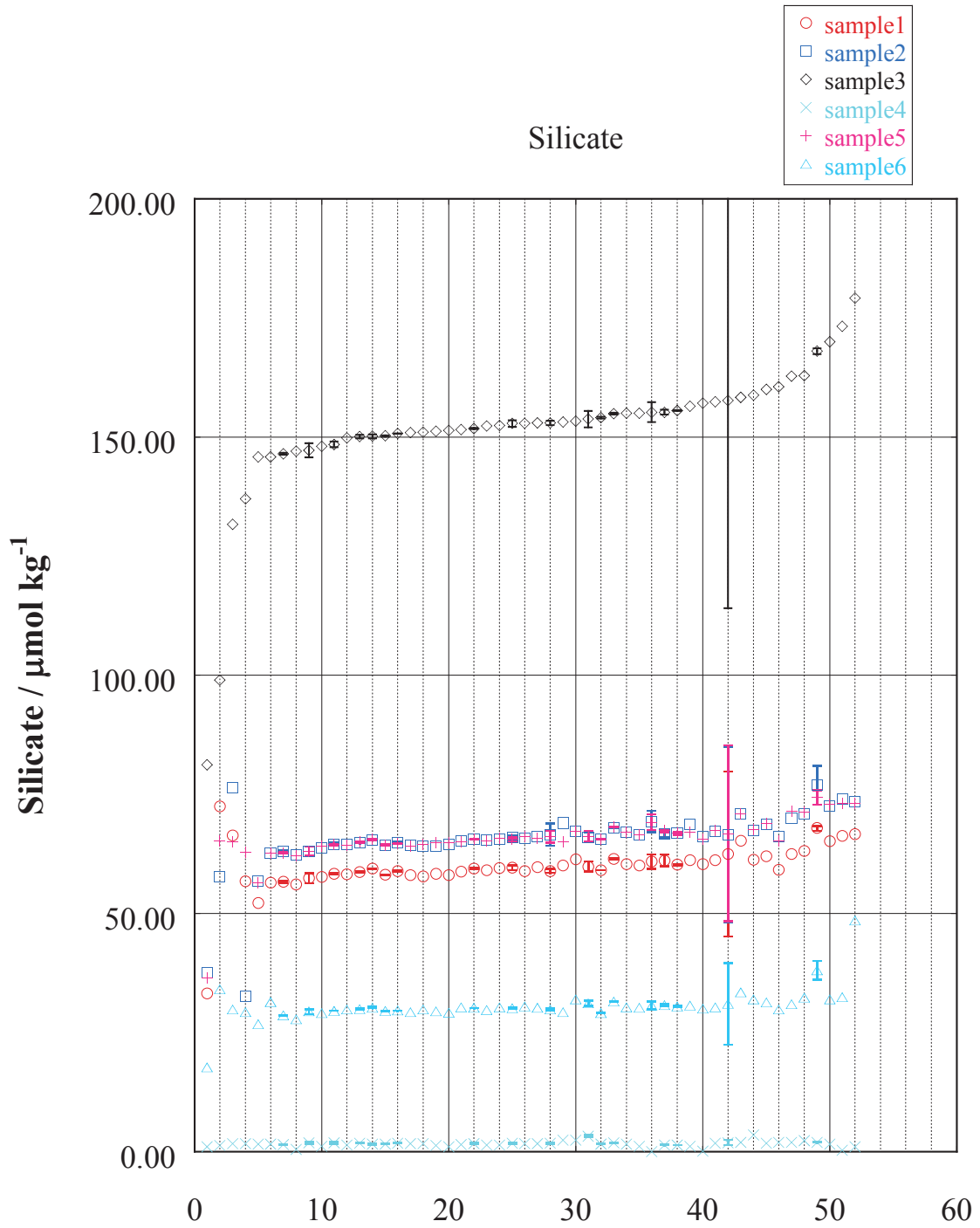


Figure 5. Silicate results for all samples. Laboratories are ranked in order of concentrations reported for Sample3

## 5.2 Consensus means, medians, and standard deviations

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

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

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

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

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

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

### 5.3 Comparison between consensus standard deviation and homogeneity of Sample3

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

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

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

### 5.5 Z-scores

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

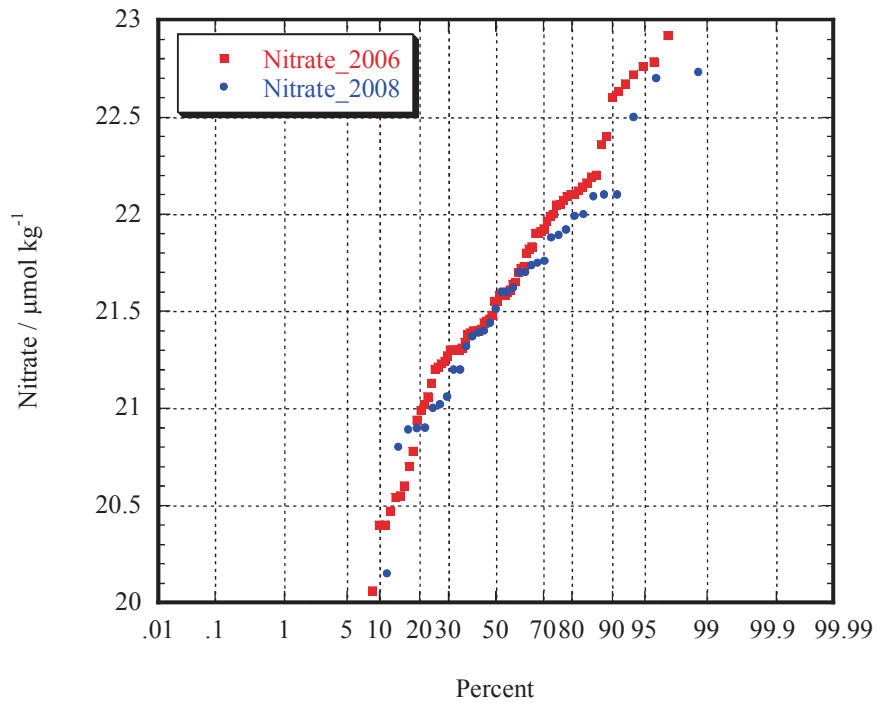


Figure 6. Cumulative distribution of reported nitrate concentrations in 2006 and 2008 I/C studies.

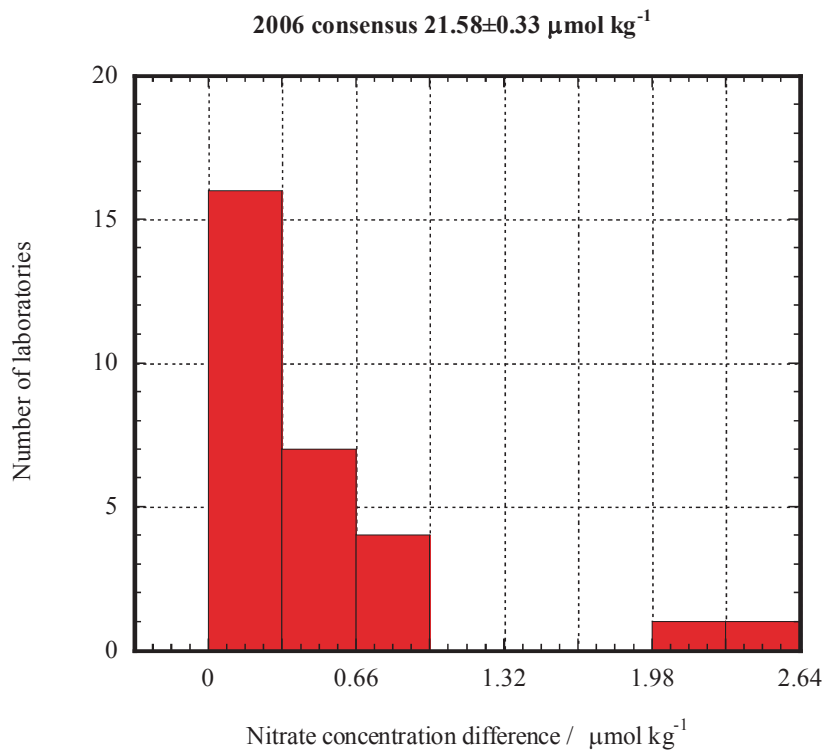


Figure 7. Comparability of nitrate concentrations measured at the same laboratory in

2006 and 2008 I/C studies.

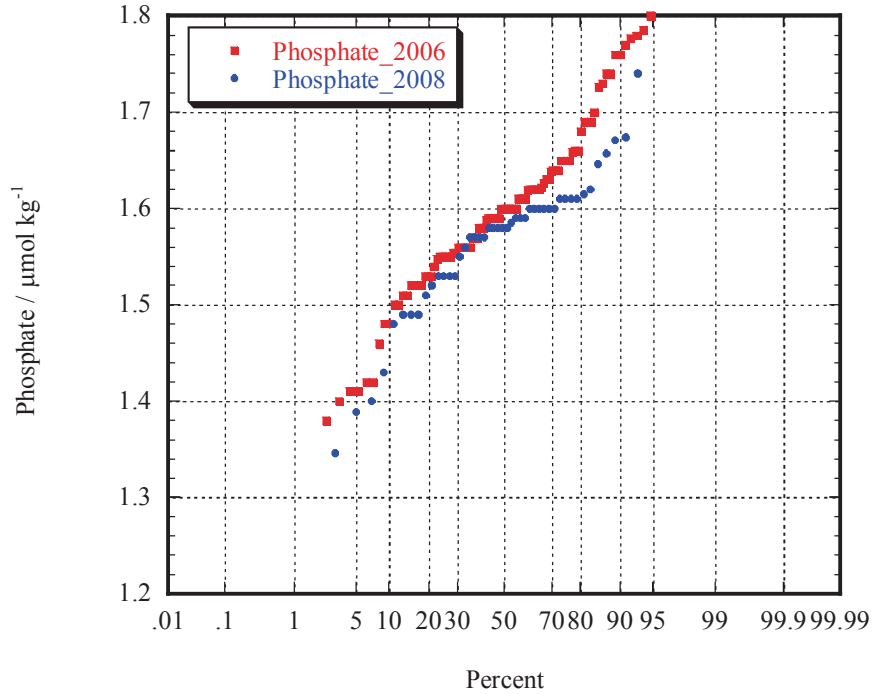


Figure 8. Cumulative distribution of reported phosphate concentrations in 2006 and 2008 I/C studies.

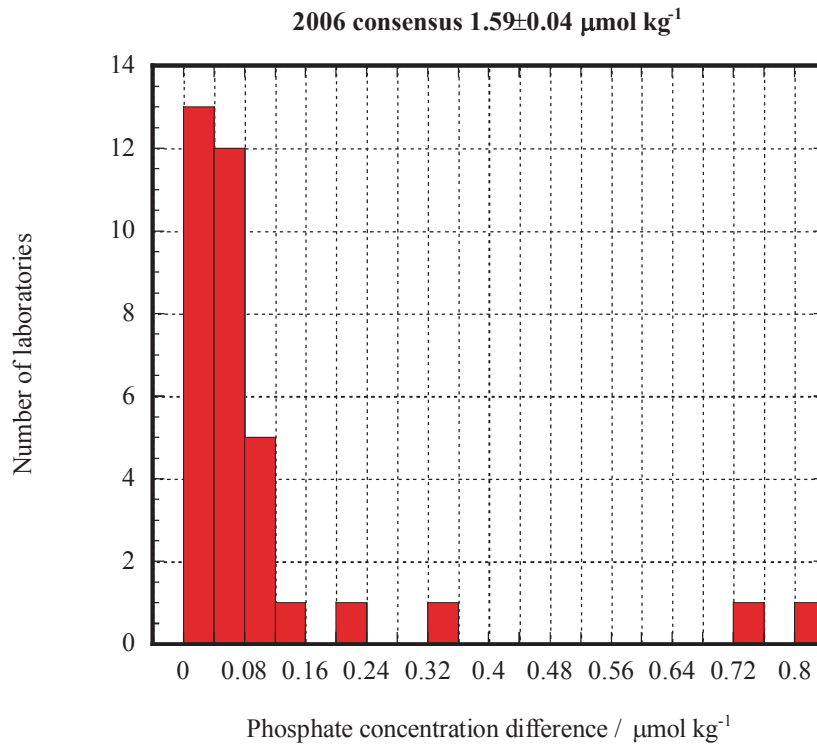


Figure 9. Comparability of phosphate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.

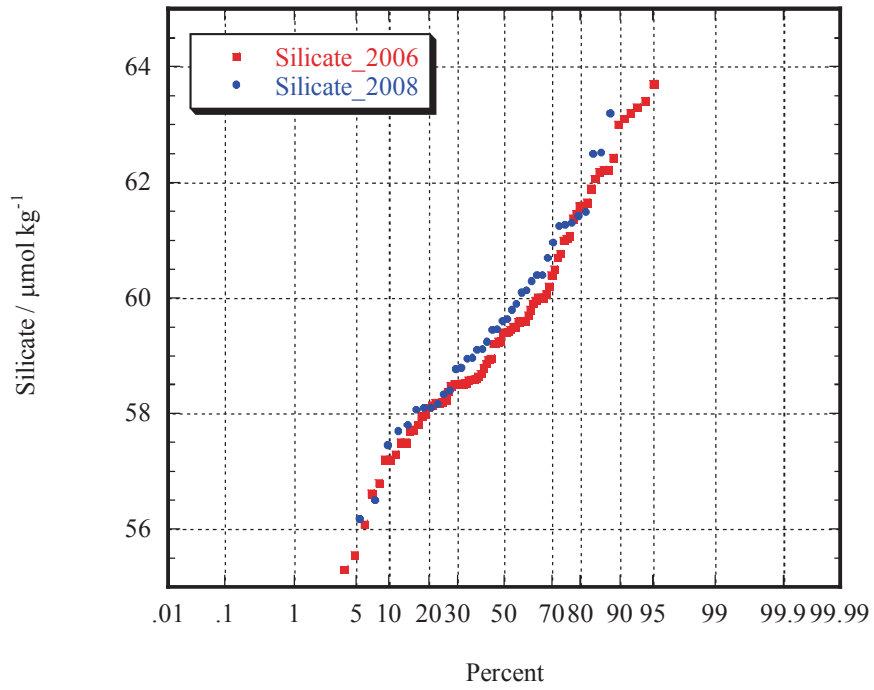


Figure 10. Cumulative distribution of reported silicate concentrations in 2006 and 2008 I/C studies.

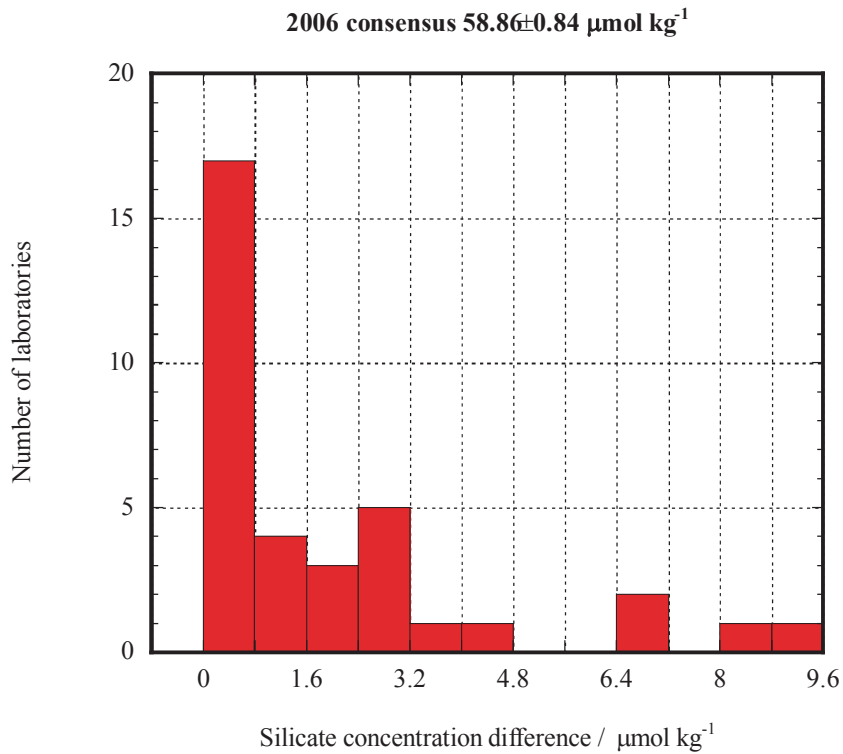


Figure 11. Comparability of silicate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.



## 7. Discussion and conclusions

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

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

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

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

## Acknowledgements

The authors express their thanks to the technical staff at all participating laboratories that conducted the analyses. The authors also thank Shoko Shimada, Sachie Ishikawa, Yukiko Suda, and Aoi Mori for preparing the many tables and figures included in this report.

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## **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, 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 Youéno	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)

Lab #	Name	Affiliation	Country
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)

Lab #	Name	Affiliation	Country
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>
68	François Baurand	Institut de Recherché pour le Développement, Campis Ifremer Technopole de Brest-Iroise	France
69	Magali Duval	Laboratoire Environnement Ressources 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 Recherché pour l'Exploitation de la Mer (IFREMER)	France
70	Dominique Munaron	Laboratoire Environnement Ressources, Institut Français de Recherché pour l'Exploitation de la Mer (IFREMER)	France
71	Patrick Raimbault	Centre d'Océanologie de Marseille - Service d'Observation	France
72	Gary Prove	Environmental Waters Laboratory, Queensland Health Forensic and Scientific Services	Australia
73	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
74	Stephen C. Coverly	SEAL Analytical GmbH	Germany
75	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.

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

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
—	32	
33	33	
34	34	
—	35	
36	36	
37	37	
38	38	13
—	39	
40	40	
42	42	
43	43	
—	44	
45	45	
46	46	
—	47	
48	48	
—	49	
50	50	
51	51	
52	52	7
53	53	
—	54	
55	55	14
56	56	
57		
58		
59		
60		
61		

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  $\mu\text{mol kg}^{-1}$ )





2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants

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

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
5	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
6	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
7	1	2008	12	9		21.9		2		21.6		2	0.352		2	1.60		2	59.8		2
	2	2008	12	9		29.9		2		29.9		2	0.033		2	2.15		2	66.2		2
	3	2008	12	9		41.36		2		41.34		2	0.016		2	2.76		2	153		2
	4	2008	12	9		0.08		2		0.06		2	0.022		2	0.03		2	1.67		2
	5	2008	12	9		29.8		2		29.8		2	0.039		2	2.15		2	65.9		2
	6	2008	12	9		6.30		2		5.67		2	0.623		2	0.48		2	30.2		2
9	8	2008	12	10				9				9			9			2			9
	1	2008	11	25	21	22.105		2		21.738		2	0.367		2	1.674		2	60.397		2
	2	2008	11	25	21	30.027		2		30.011		2	0.017		2	2.275		2	66.165		2
	3	2008	11	25	21	40.854		2		40.850		2	0.004		2	3.002		2	157.158		2
	4	2008	11	25	21	0.032		2		0.008		2	0.024		2	0.073		2	0.149		2
	5	2008	11	25	21	29.897		2		29.878		2	0.020		2	2.311		2	65.731		2
6	2008	11	25	21	6.108		2		5.451		2	0.657		2	0.550		2	30.010		2	

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	
<b>10</b>	1	2008	11	11	20			9	20.9	0.1	2	0.37	0	1.55	0.01	2	58.4	0.1	2			
	2	2008	11	11	20			9	28.9	0.1	2	0.02	0	2.09	0.01	2	64.6	0.3	2			
	3	2008	11	11	20			9	40.1	0.1	2	0.00	0	2.69	0.01	2	148.5	0.6	2			
	4	2008	11	11	20			9	0.0	0.1	2	0.00	0	0.08	0.01	2	1.9	0.2	2			
	5	2008	11	11	20			9	28.9	0.2	2	0.02	0	2.09	0.01	2	64.5	0.2	2			
	6	2008	11	11	20			9	5.6	0.1	2	0.66	0	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	1.56	0.01	2						
	2	2009	1	9	17.6	30.5	0.1	2	30.5	0.1	2	0.03	0.00	2.15	0.00	2						
	3	2009	1	9	17.6	41.4	0.1	2	41.4	0.1	2	0.01	0.00	2.80	0.00	2						
	4	2009	1	9	17.6	0.1	0.1	2	0.1	0.1	2	0.02	0.00	0.03	0.01	2						
	5	2009	1	9	17.6	30.4	0.1	2	30.4	0.1	2	0.03	0.00	2.14	0.01	2						
	6	2009	1	9	17.6	6.6	0.1	2	6.0	0.1	2	0.59	0.00	0.44	0.01	2						
<b>13</b>	1	2008	10	16	0	22.35		2	21.99		2	0.36	2	1.53		2						
	2	2008	10	16	0	30.27		2	30.25		2	0.03	2	2.12		2						
	3	2008	10	16	0	41.58		2	41.57		2	0.01	2	2.77		2						
	4	2008	10	16	0	0.01		2	0.00		2	0.02	2	0.01		2						
	5	2008	10	16	0	30.29		2	30.26		2	0.03	2	2.11		2						
	6	2008	10	16	0	6.42		2	5.79		2	0.63	2	0.43		2						
<b>14</b>	1	2008	12	31	22.2	22.27	0.13	2	21.92		2	0.35	0.00	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	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	2.69	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	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	2.03	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	0.45	0.02	2	31.54	0.04	2			

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

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

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
23	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	<0.034		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	
24	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	
25	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	
26	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	

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

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

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	
33	1	2008	11	5	21.3	22.50	0.23	2	22.09	0.23	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	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	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	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	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	0.66	0.01	2	0.55	0.01	2	29.87	0.14	2			
34	1	2009	1	12		22.469		2	22.112		0.450		2	1.659		2	56.769		2			
	2	2009	1	12		30.226		2	30.145		0.102		2	2.252		2	32.724		2			
	3	2009	1	12		41.251		2	41.200		0.065		2	2.958		2	137.071		2			
	4	2009	1	12		0.314		2	0.249		0.083		2	0.057		2	1.731		2			
	5	2009	1	12		30.359		2	30.283		0.097		2	2.233		2	62.843		2			
	6	2009	1	12		6.678		2	6.103		0.703		2	0.562		2	29.327		2			
36	1	2008	10		22			9	21.37		0.37		2	1.61		2	61.42		2			
	2	2008	10		22			9	29.56		0.05		2	2.15		2	67.24		2			
	3	2008	10		22			9	40.96		0.03		2	2.88		2	153.35		2			
	4	2008	10		22			9	0.16		0.00		2	0.03		2	2.44		2			
	5	2008	10		22			9	29.55		0.04		2	2.16		2	67.29		2			
	6	2008	10		22			9	5.68		0.66		2	0.50		2	32.01		2			
37	1	2009	1			21.73	0.33	2	21.42	0.33	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	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	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	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	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	0.59	0.01	2	0.49	0.01	2	30.80	0.22	2			

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
38	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
40	1	2008	11	17	25.5			9				9			9	1.60	0.02	2			9
	2	2008	11	17	25.5			9				9			9	2.19	0.00	2			9
	3	2008	11	17	25.5			9				9			9	2.90	0.00	2			9
	4	2008	11	17	25.5			9				9			9	0.02	0.01	2			9
	5	2008	11	17	25.5			9				9			9	2.19	0.01	2			9
	6	2008	11	17	25.5			9				9			9	0.50	0.00	2			9
42	1	2008	10	16	22	23.04		2		22.73		2	0.32		2	1.53		2	52.30		2
	2	2008	10	16	22	30.99		2		30.98		2	0.00		2	2.03		2	56.76		2
	3	2008	10	16	22	41.88		2		41.87		2	0.00		2	2.80		2	145.84		2
	4	2008	10	16	22	0.00		2		0.00		2	0.00		2	0.01		2	1.58		2
	5	2008	10	16	22	31.11		2		31.11		2	0.00		2	2.34		2	56.42		2
	6	2008	10	16	22	6.72		2		6.13		2	0.60		2	0.41		2	26.84		2
	7	2008	11	6	22	33.49		2		33.36		2	0.12		2	3.21		2	258.38		2
	8	2008	11	6	22			9				9			9			9			9
43	1	2008	11	7	23	22.104	0.200	2		21.749	0.220	2	0.356	0.020	2	1.808	0.050	2	57.459	1.000	2
	2	2008	11	7	23	29.917	0.200	2		29.894	0.220	2	0.022	0.020	2	2.371	0.050	2	63.078	1.000	2
	3	2008	11	7	23	40.989	0.200	2		40.980	0.220	2	0.009	0.020	2	3.242	0.050	2	147.269	1.500	2
	4	2008	11	7	23	0.000	0.020	2		0.000	0.040	2	0.012	0.020	2	0.041	0.020	2	1.900	0.200	2
	5	2008	11	7	23	29.917	0.200	2		29.894	0.220	2	0.022	0.020	2	2.371	0.050	2	63.078	1.000	2
	6	2008	11	7	23	6.326	0.200	2		5.682	0.220	2	0.645	0.020	2	0.655	0.020	2	29.468	0.500	2



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

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
45	1	2008	10	21	22	22.115	2.943	2		21.76	0.050	2	0.352	0.188	2	1.671	0.188	2	62.521	17.282	2
	2	2008	10	21	22	30.242	4.025	2				9	<0.06	0.253	2	2.250	0.253	2	66.659	18.424	2
	3	2008	10	21	22	42.196	5.617	2				9	<0.06	0.322	2	2.862	0.322	2	157.76	43.61	2
	4	2008	10	21	22	<0.24		5				9	<0.06	0.022	2	0.196	0.022	2	1.896	0.524	2
	5	2008	10	21	22	29.829	3.970	2				9	<0.06	0.030	2	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
46	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
48	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
50	1	2008	12	3	22	21.55		2		21.02		2	0.54		2	2.15		2	72.53		2
	2	2008	12	3	22	24.45		2		24.34		2	0.11		2	2.74		2	57.87		2
	3	2008	12	3	22	37.47		2		37.24		2	0.23		2	3.32		2	99.01		2
	4	2008	12	3	22	0.18		2				9	0.18		2	0.32		2	1.37		2
	5	2008	12	3	22	27.06		2		26.88		2	0.18		2	2.84		2	65.21		2
	6	2008	12	3	22	5.13		2		4.20		2	0.93		2	0.85		2	34.11		2

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
51	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		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
52	1	2009	1	16	22.3	22.23	0.04	2		21.89	0.04	2	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
53	1	2008				21.42		2		21.06		2	0.36		2	1.57		2	61.31		2
	2	2008				29.92		2		29.89		2	0.04		2	2.17		2	67.56		2
	3	2008				41.46		2		41.44		2	0.02		2	2.81		2	158.86		2
	4	2008				0.03		2		0.01		2	0.02		2	0.01		2	3.61		2
	5	2008				30.02		2		29.98		2	0.04		2	2.17		2	67.76		2
	6	2008				6.21		2		5.56		2	0.64		2	0.46		2	31.97		2
55	1	2008	1	6		22.24	0.04	2		21.88	0.04	2	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	2	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	2	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	2	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	2	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	2	0.63	0.00	2	0.46	0.00	2	30.19	0.04	2

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
<b>56</b>	1				25.4	21.70	0.08	2				9			9	1.57	0.00	2	58.98	0.05	2
	2				25.4	29.69	0.08	2				9			9	2.18	0.01	2	64.96	0.06	2
	3				25.4	41.05	0.21	2				9			9	2.79	0.00	2	150.79	0.03	2
	4				25.4	0.08	0.02	2				9			9	0.00	0.00	2	1.77	0.00	2
	5				25.4	29.62	0.10	2				9			9	2.15	0.01	2	64.75	0.04	2
	6				25.4	6.17	0.03	2				9			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

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
64	1					19.355		2		19.355		2	0.000		2	1.042		2	33.333		2
	2					22.798		2		22.581		2	0.217		2	3.125		2	37.500		2
	3					48.387		2		48.387		2	0.000		2	3.125		2	81.250		2
	4					0.435		2		0.000		2	0.435		2	3.125		2	1.042		2
	5					24.411		2		24.194		2	0.217		2	2.083		2	36.458		2
	6					7.104		2		6.452		2	0.652		2	0.000		2	17.708		2
65	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
66	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
68	8	2008	12	1	22.5			9				9			9						9
	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	

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	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		0.08	9	<0.10		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			9			2	
	8	2008	12	1	20			9				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	

2008 RMNS Intercomparison Exercise

Table A3 Results reported by the participants (continued)

Lab	Sample	Year	Month	Day	Temperature	NOX	ERR	Flag	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag	
<b>71-2</b>																						
	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	273.3		9	273.3		2	
	8	2008	11	4	19			9				9			9	2.88		9	2.88		2	
<b>72</b>																						
	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	
<b>73</b>																						
	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	
<b>74</b>																						
	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		2		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	Reduct	Nitrate	ERR	Flag	Nitrite	ERR	Flag	Phosphate	ERR	Flag	Silicate	ERR	Flag
	1	2009	1	9	16.2	22.40		2				9	0.373		2	1.387		2	58.247		2
	2	2009	1	9	16.2	30.67		2				9	0.042		2	1.970		2	64.620		2
	3	2009	1	9	16.2	42.39		2				9	0.030		2	2.667		2	149.90		2
	4	2009	1	9	16.2	0.07		2				9	0.030		2	0.044		2	1.43		2
	5	2009	1	9	16.2	30.64		2				9	0.051		2	1.96		2	64.43		2
	6	2009	1	9	16.2	7.07		2				9	0.679		2	0.401		2	29.9		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  $\mu\text{mol kg}^{-1}$ .**

<b>Lab</b>	<b>Sample</b>	<b>DOC</b>	<b>Error</b>
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

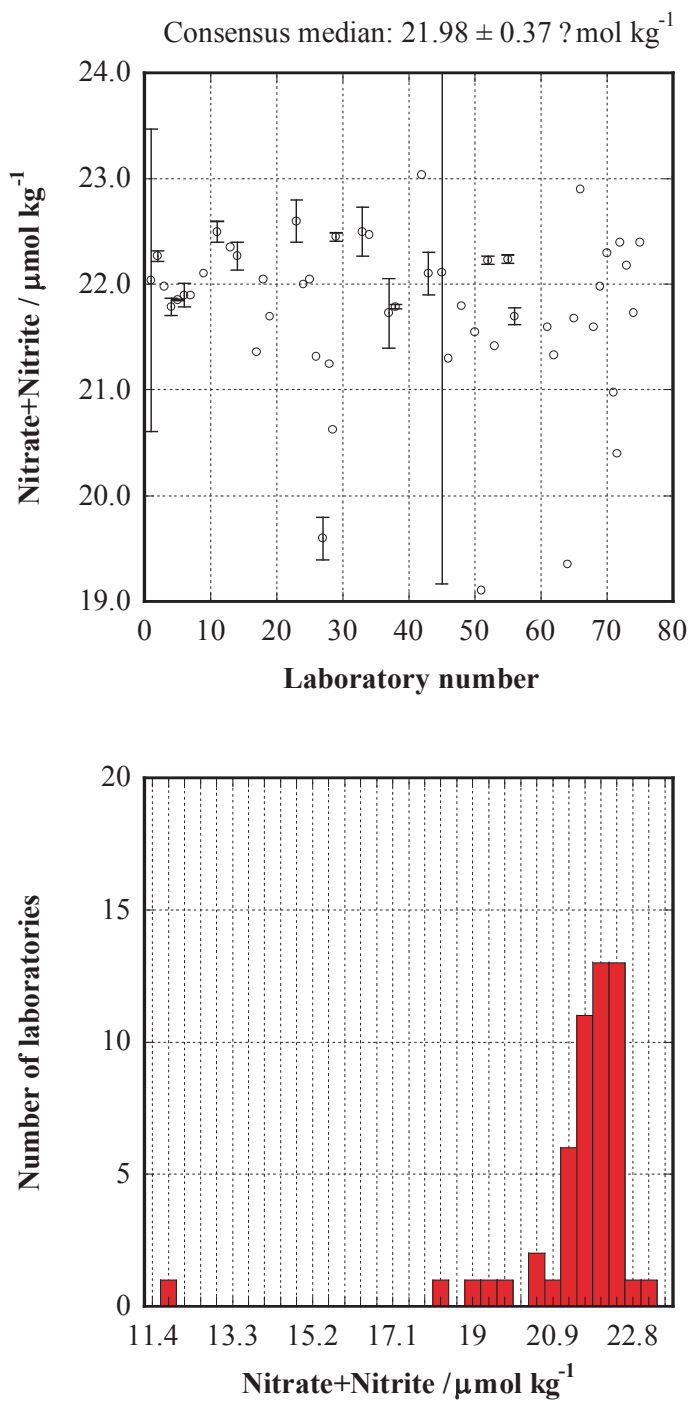


Figure A1-1 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #1 (lower panel)

## Sample 2 Nitrate+Nitrite

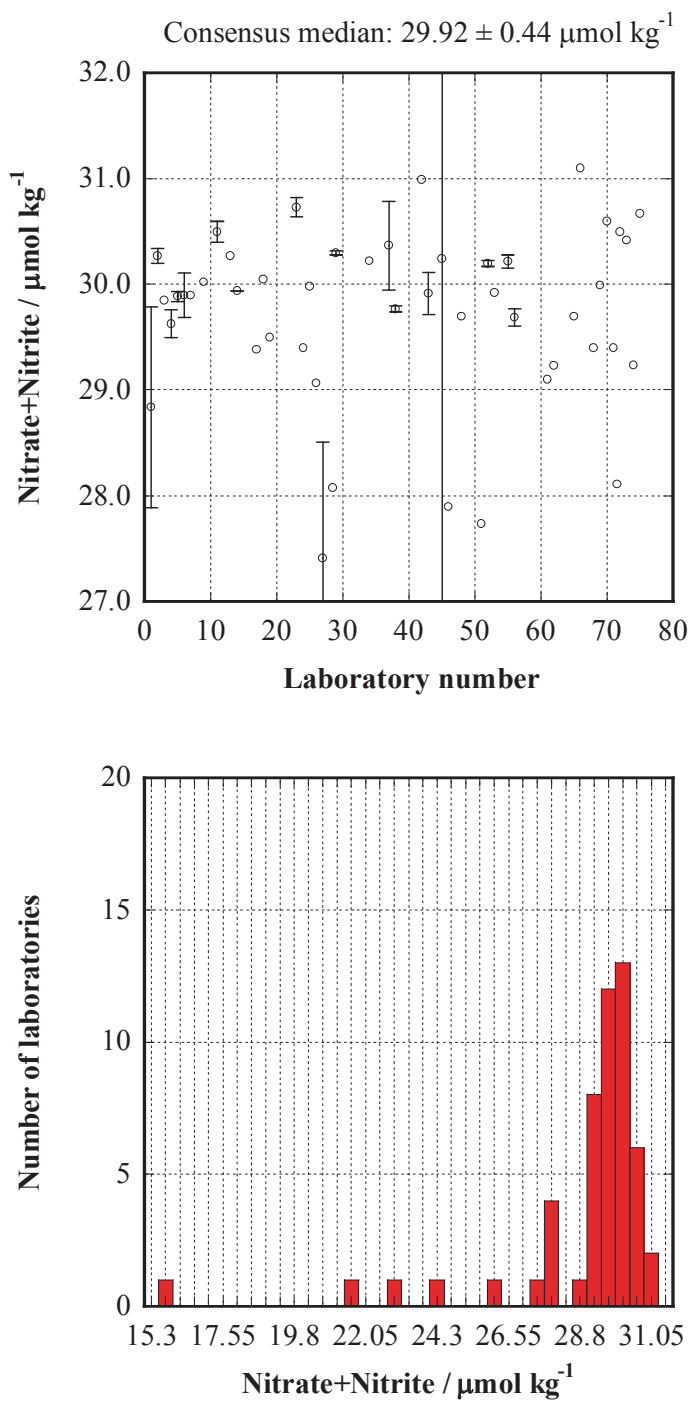


Figure A1-2 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #2 (lower panel)

### Sample 3 Nitrate+Nitrite

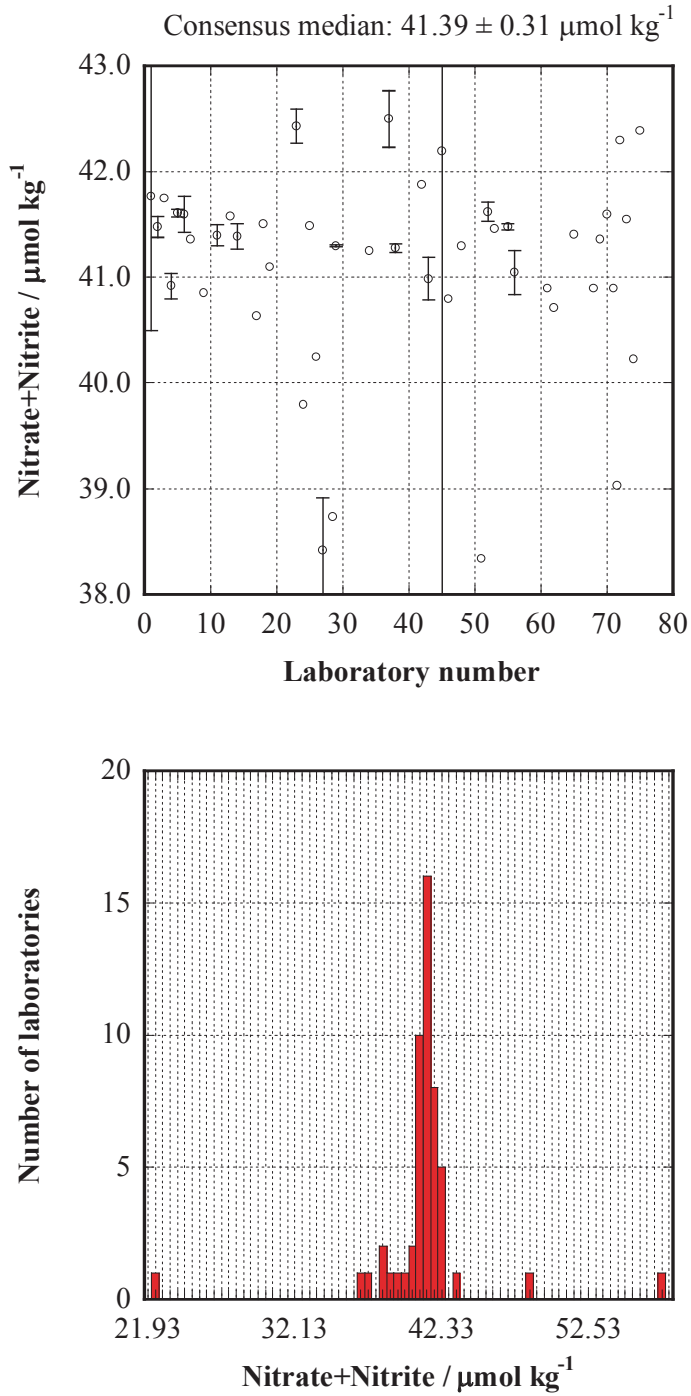


Figure A1-3 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #3 (lower panel)

## Sample 4 Nitrate+Nitrite

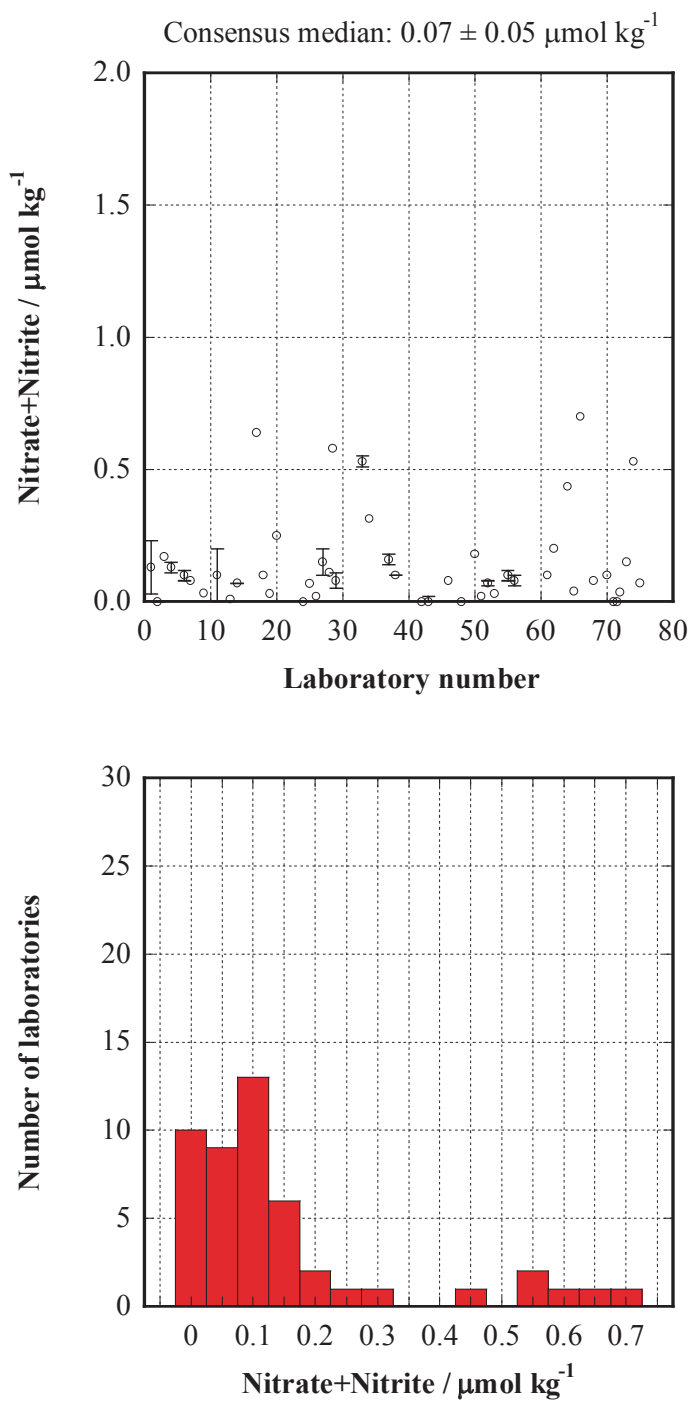


Figure A1-4 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #4 (lower panel)

## Sample 5 Nitrate+Nitrite

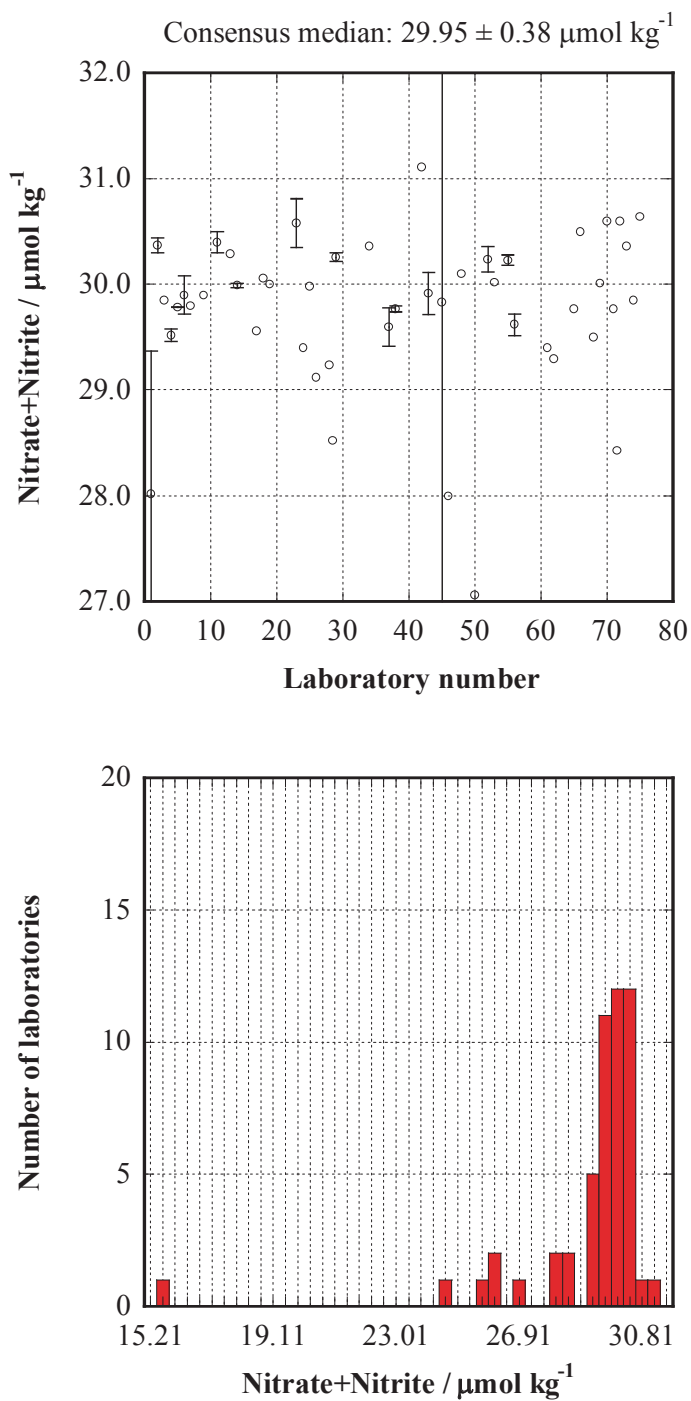


Figure A1-5 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #5 (lower panel)

## Sample 6 Nitrate+Nitrite

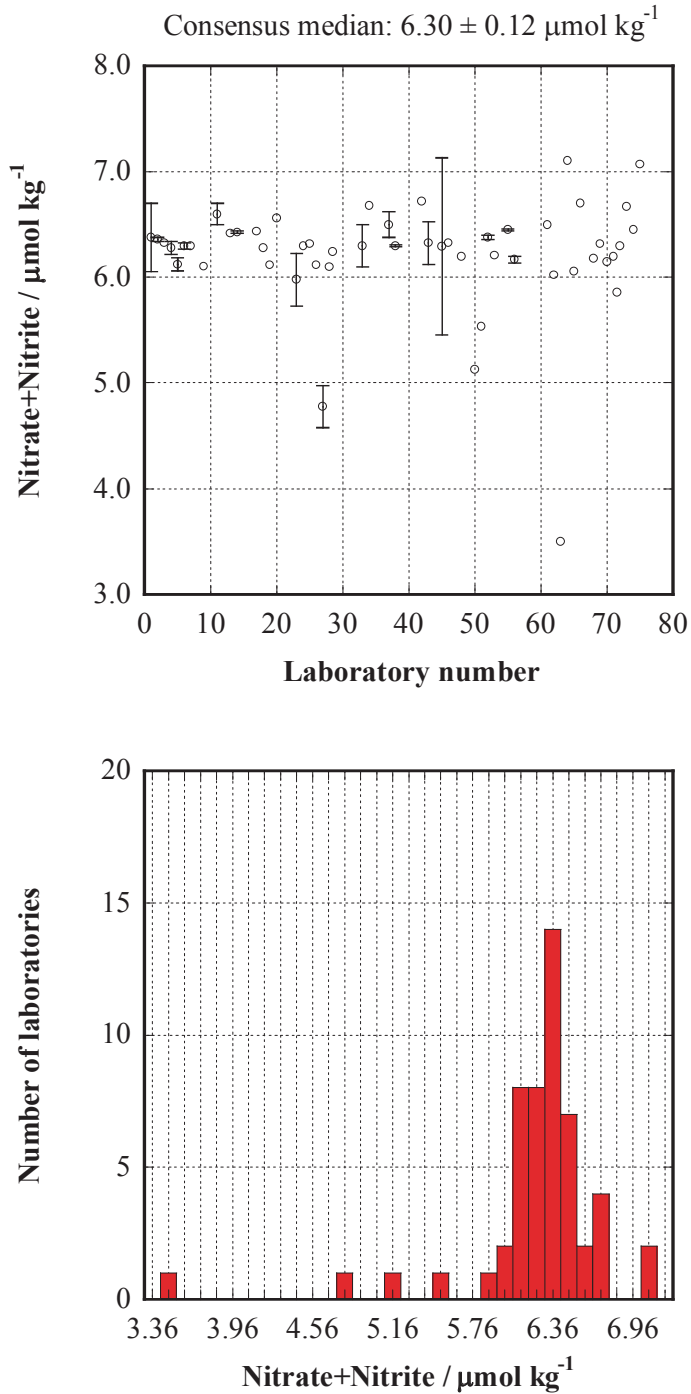


Figure A1-6 Nitrate+nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate+nitrite concentration for sample #6 (lower panel)

## Sample 1 Nitrate

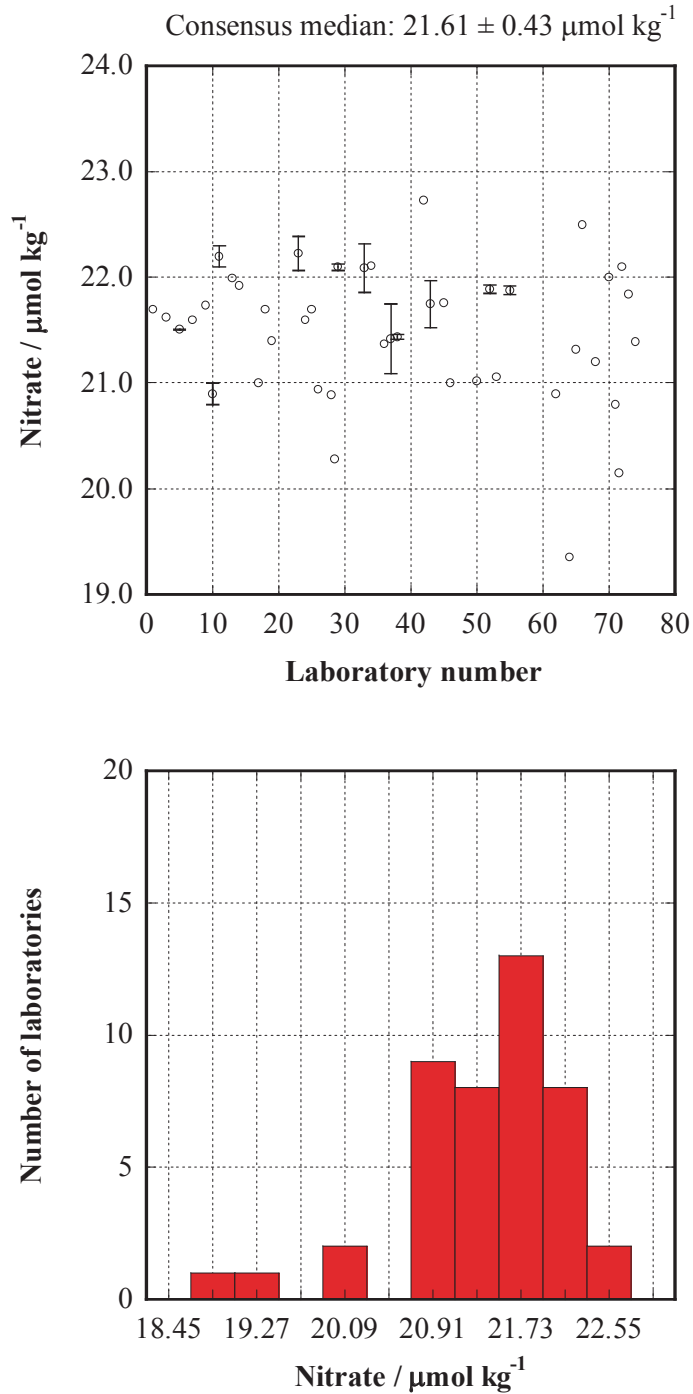


Figure A2-1 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #1 (lower panel)

## Sample 2 Nitrate

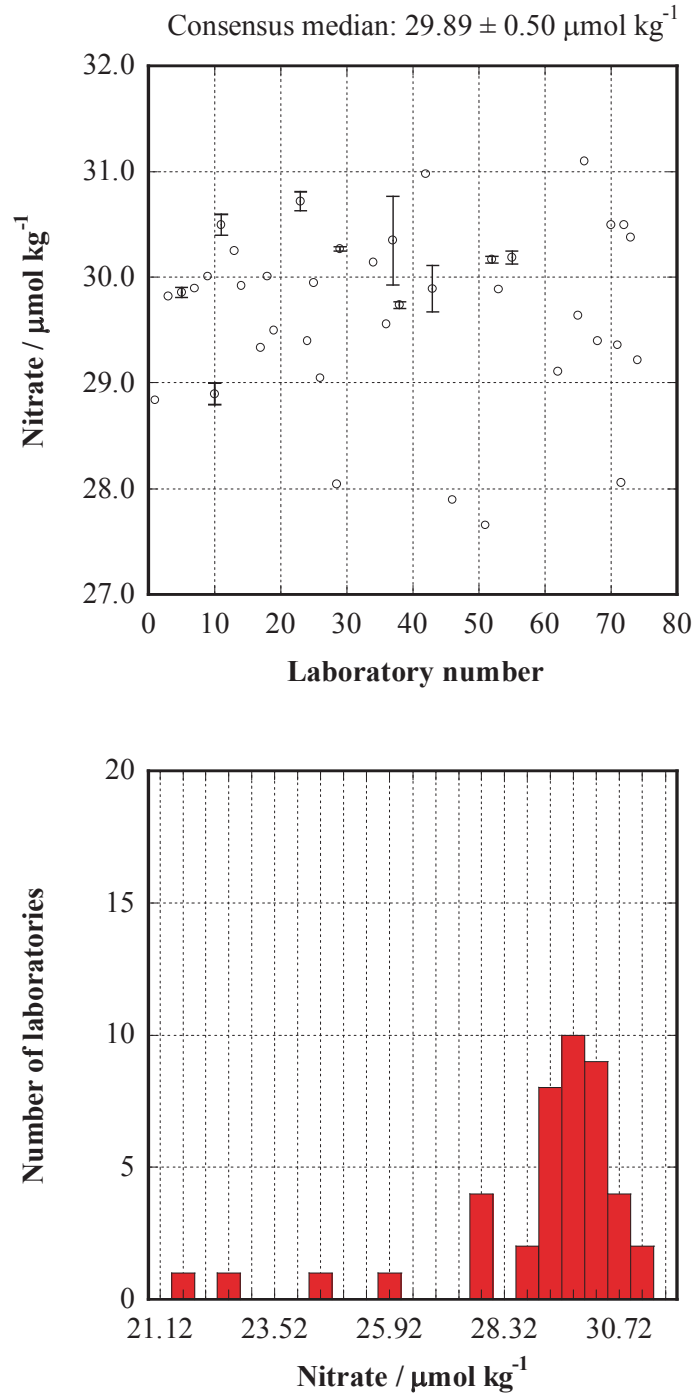


Figure A2-2 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #2 (lower panel)



### Sample 3 Nitrate

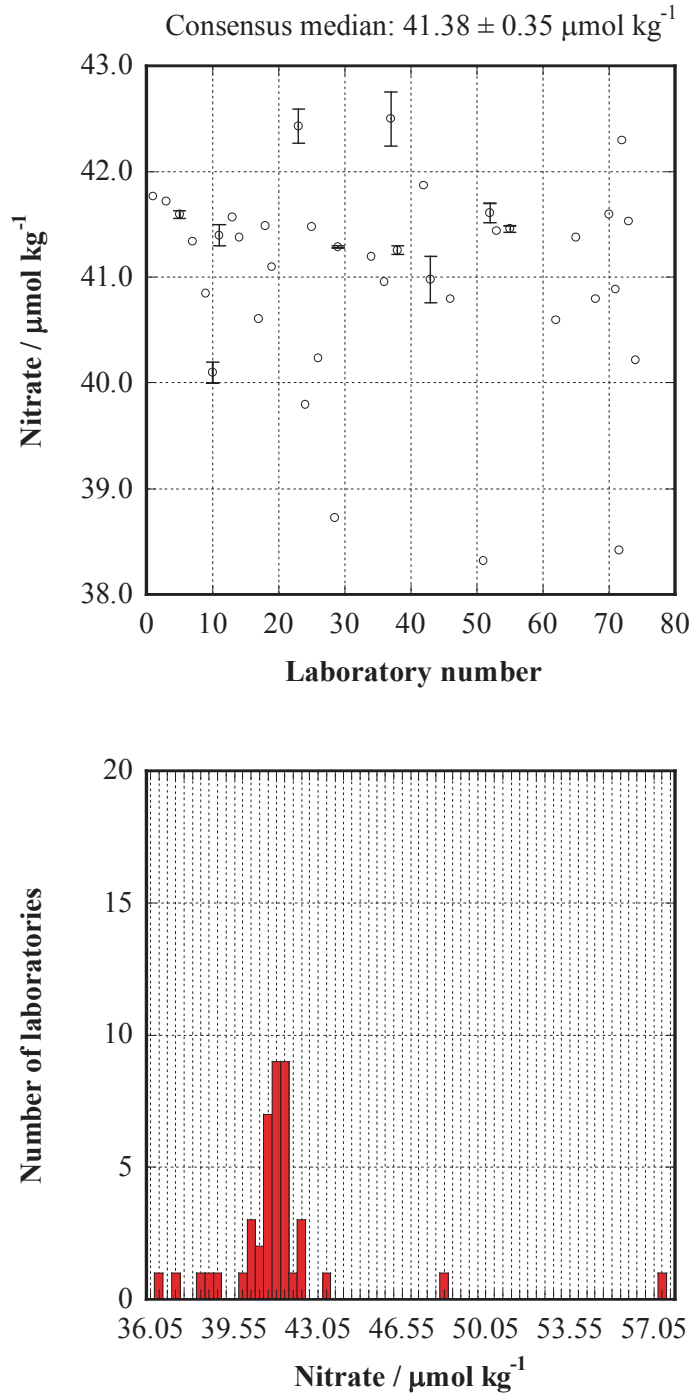


Figure A2-3 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #3 (lower panel)

## Sample 4 Nitrate

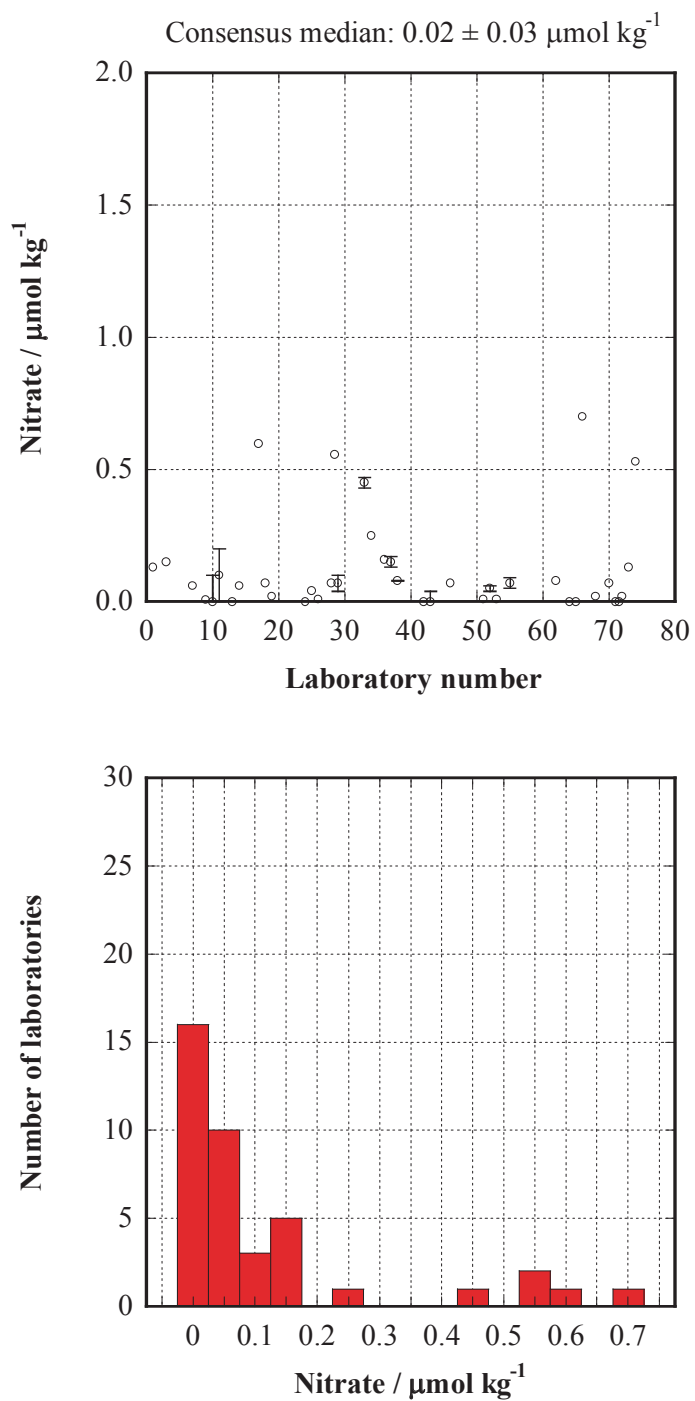


Figure A2-4 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #4 (lower panel)

## Sample 5 Nitrate

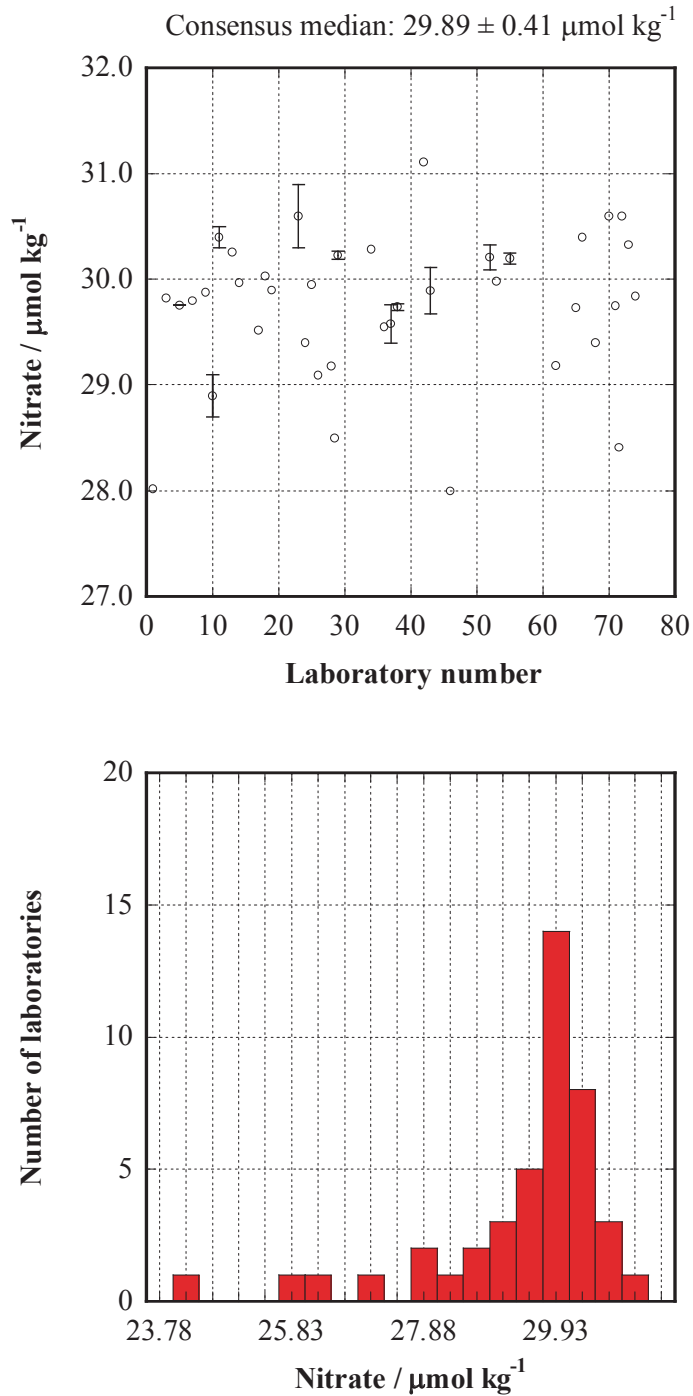


Figure A2-5 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #5 (lower panel)

## Sample 6 Nitrate

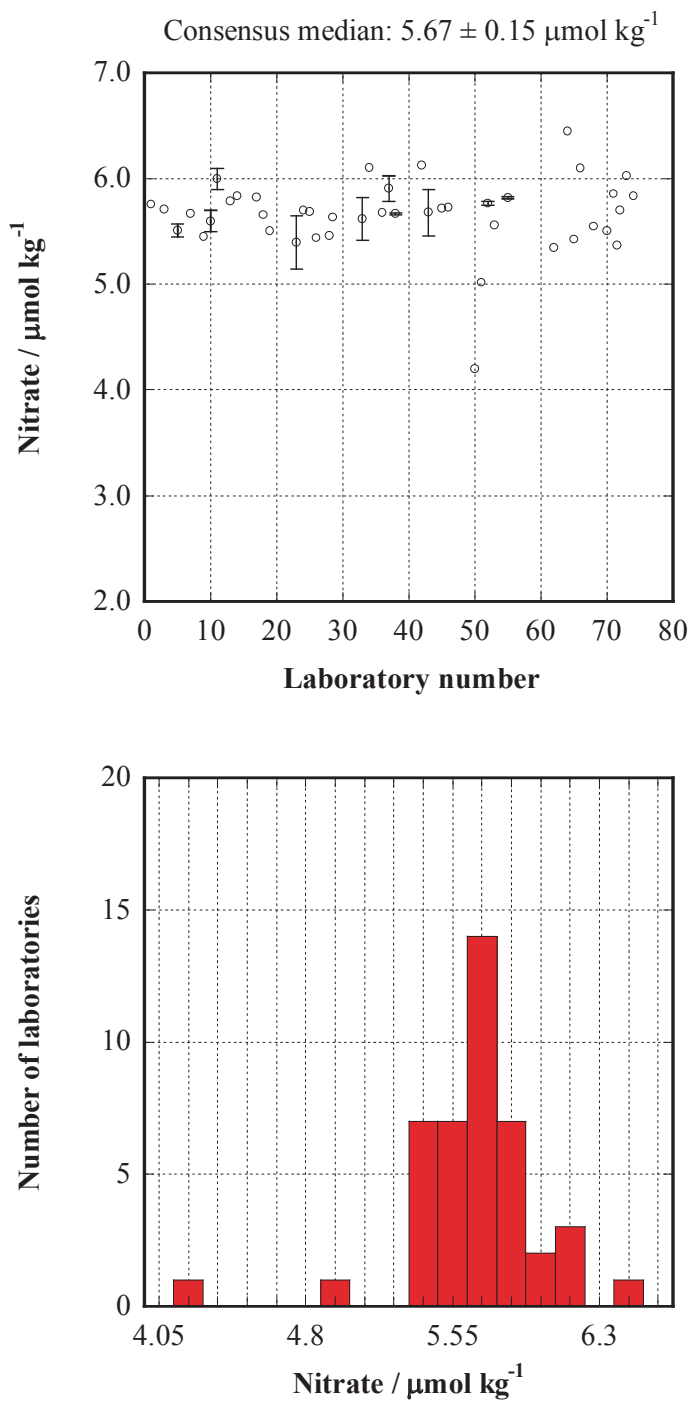


Figure A2-6 Nitrate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrate concentration for sample #6 (lower panel)

## Sample 1 Nitrite

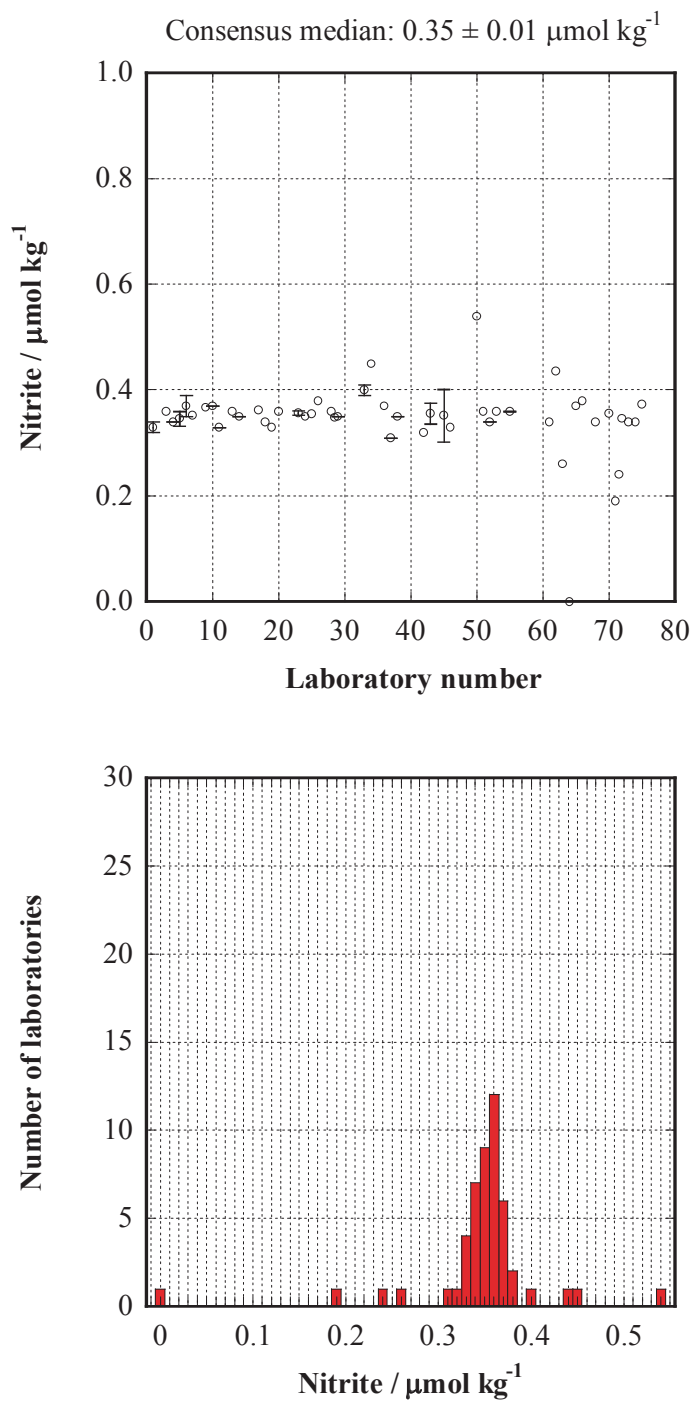


Figure A3-1 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #1 (lower panel)

## Sample 2 Nitrite

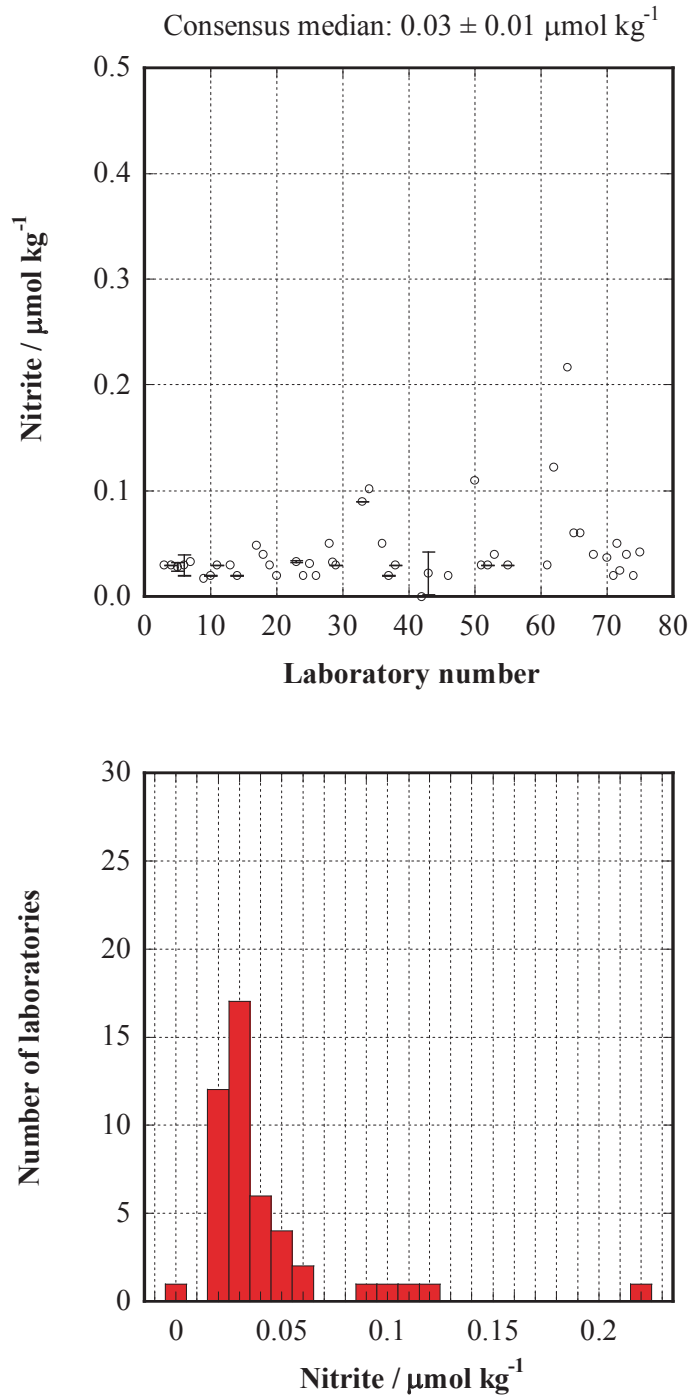


Figure A3-2 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #2 (lower panel)

## Sample 3 Nitrite

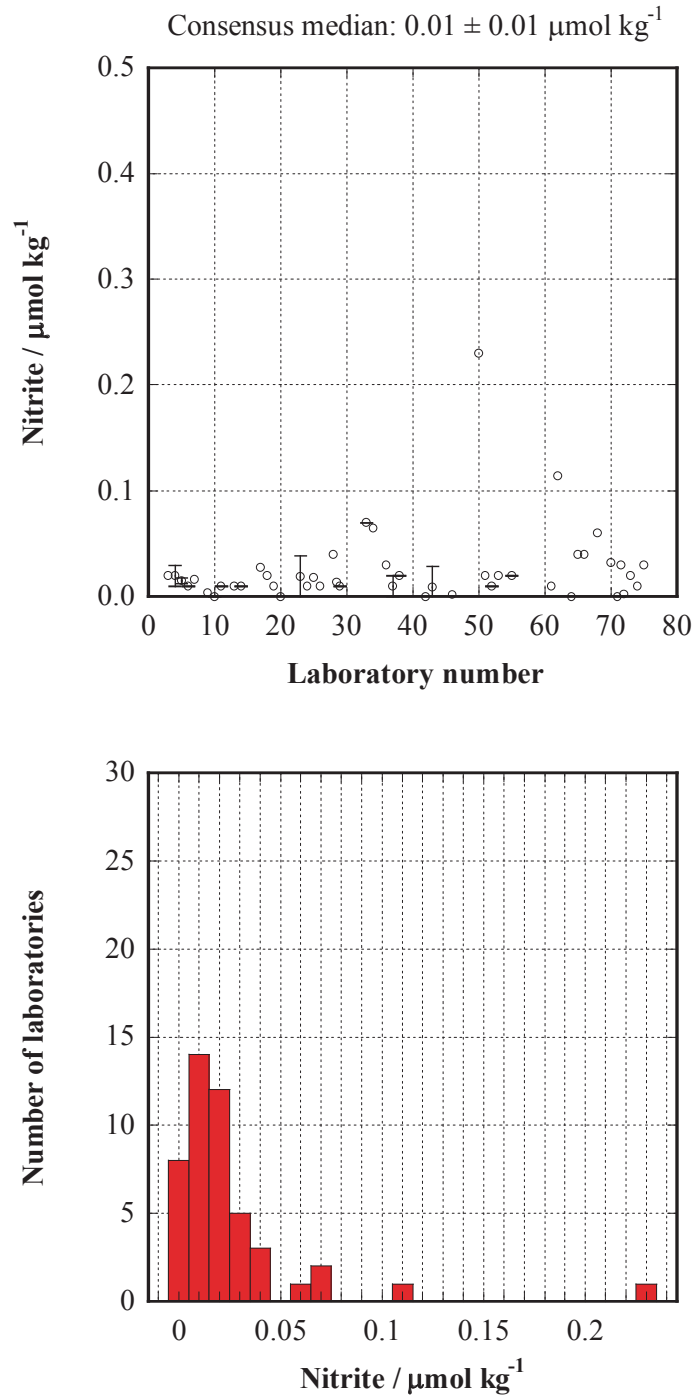


Figure A3-3 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #3 (lower panel)

## Sample 4 Nitrite

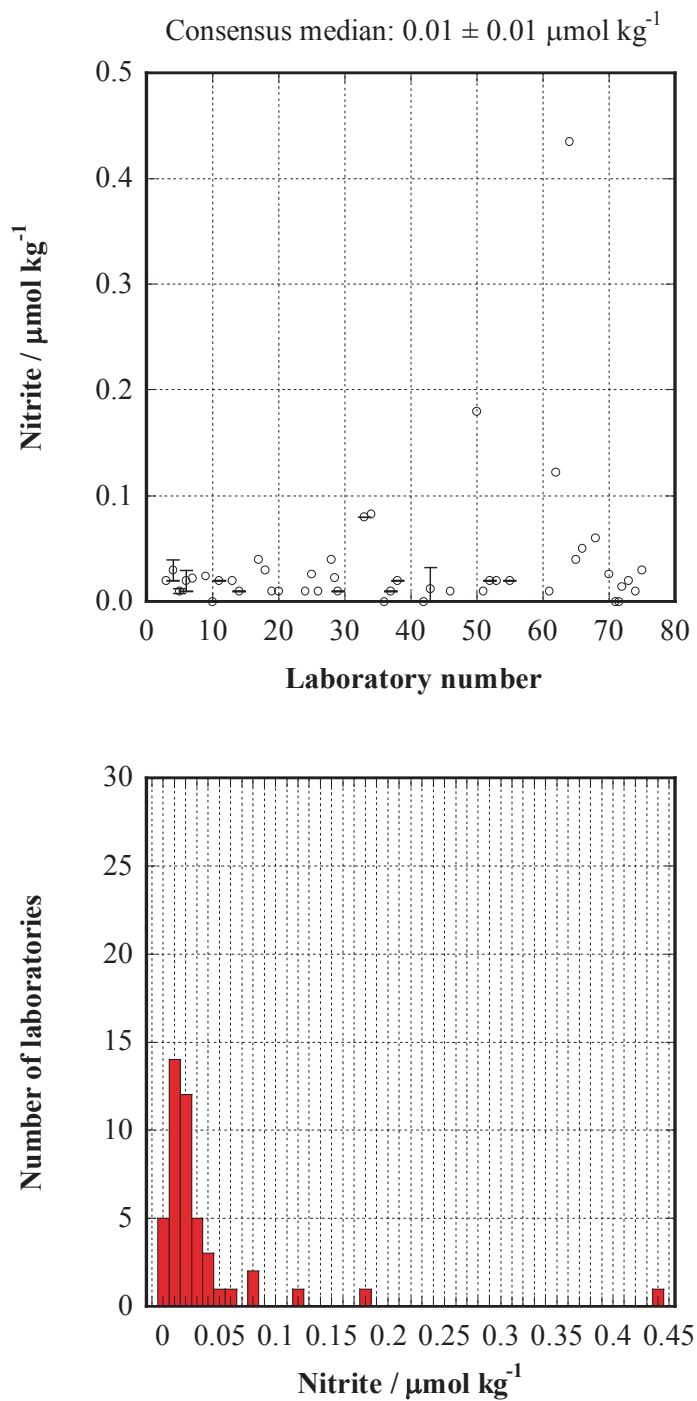


Figure A3-4 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #4 (lower panel)



## Sample 5 Nitrite

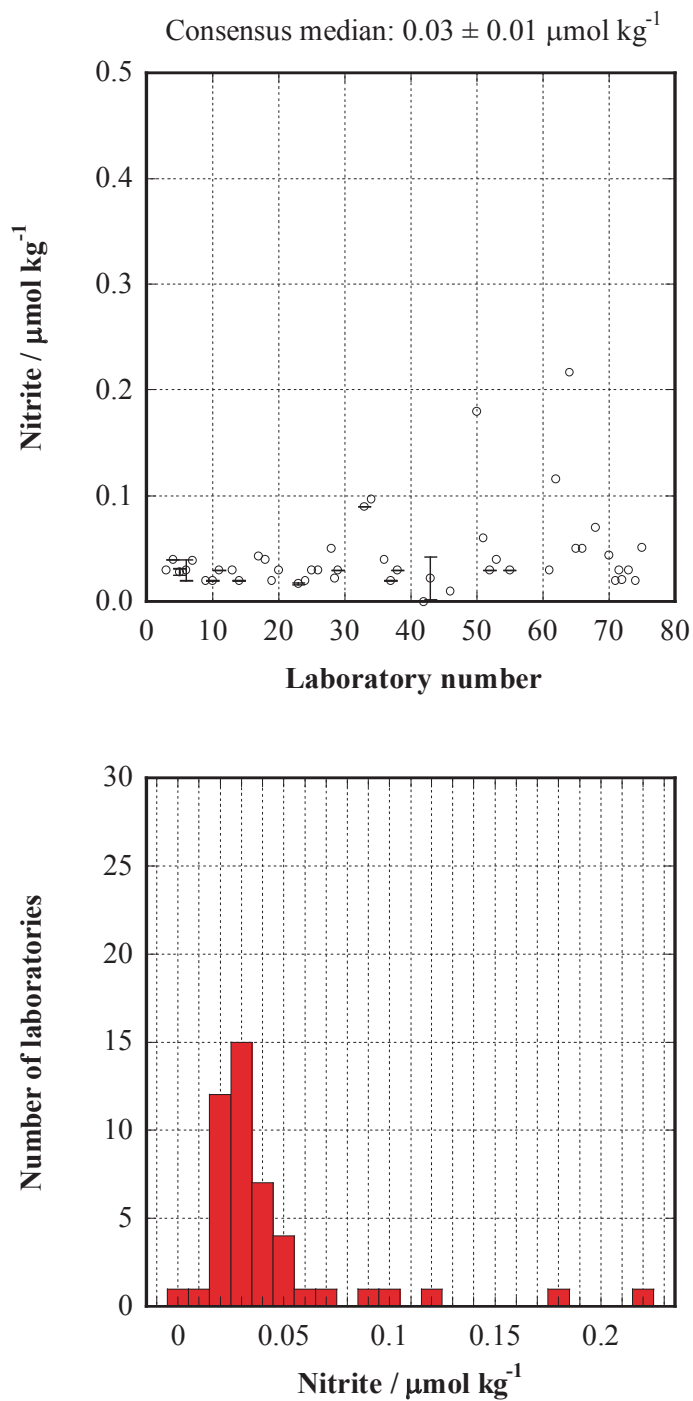


Figure A3-5 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #5 (lower panel)

## Sample 6 Nitrite

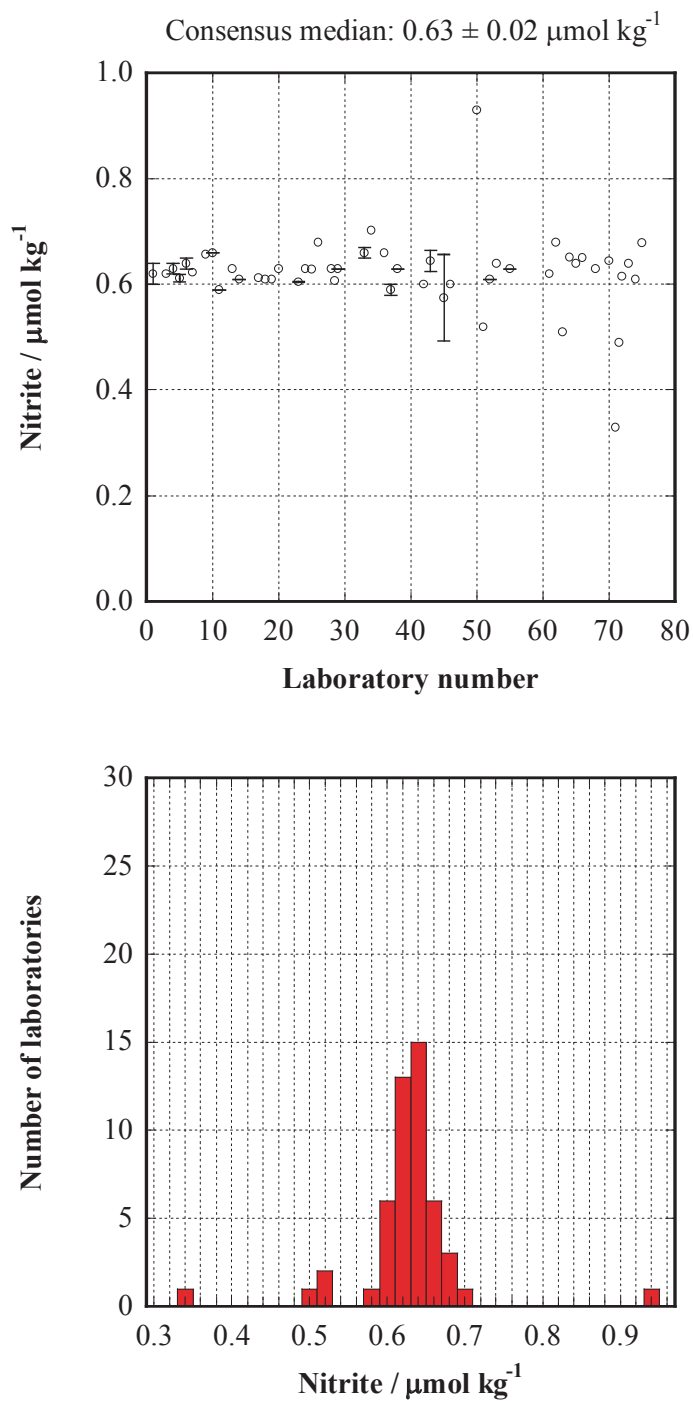


Figure A3-6 Nitrite: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported nitrite concentration for sample #6 (lower panel)

## Sample 1 Phosphate

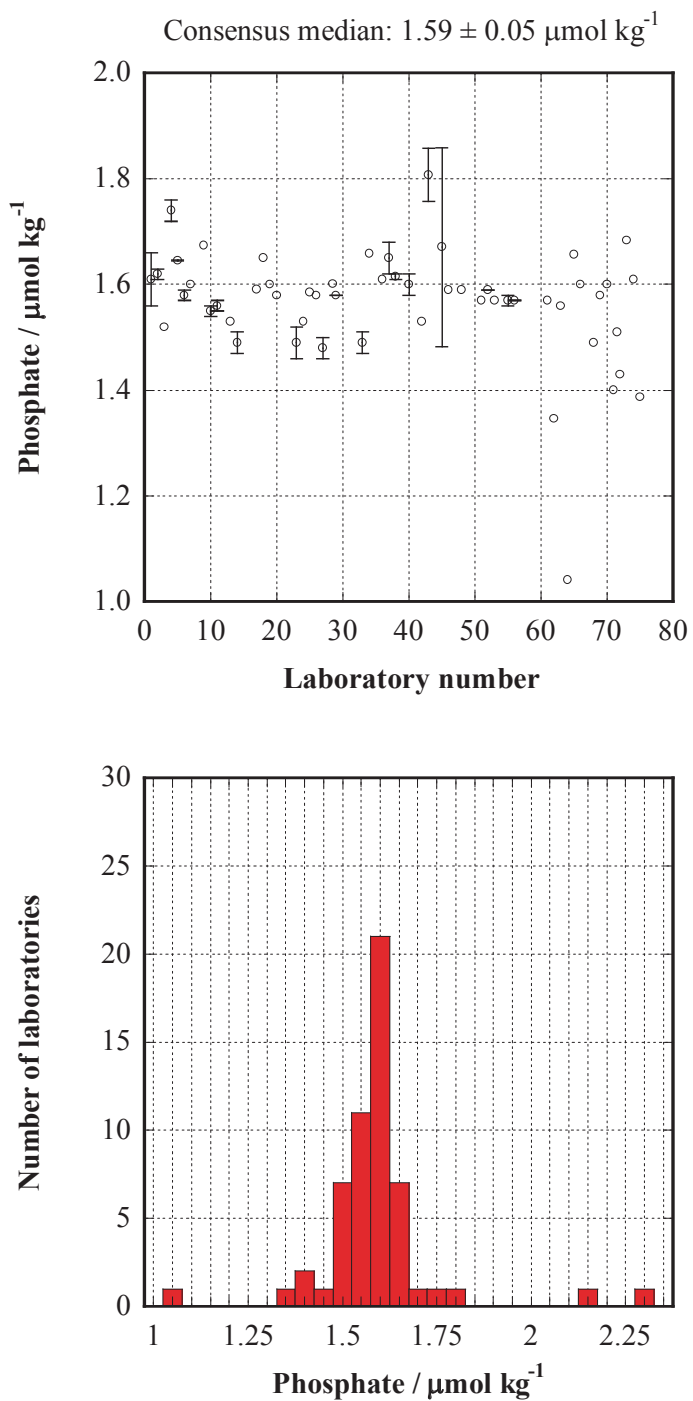


Figure A4-1 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #1 (lower panel)

## Sample 2 Phosphate

Consensus median:  $2.16 \pm 0.04 \mu\text{mol kg}^{-1}$

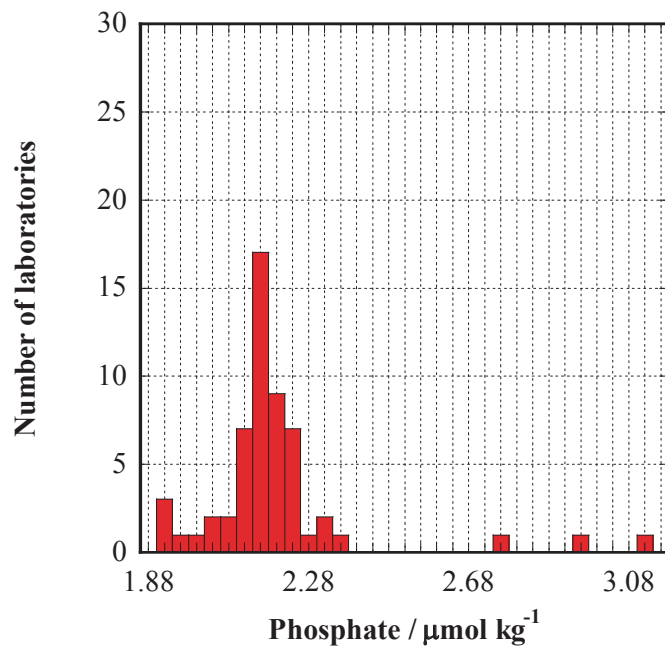
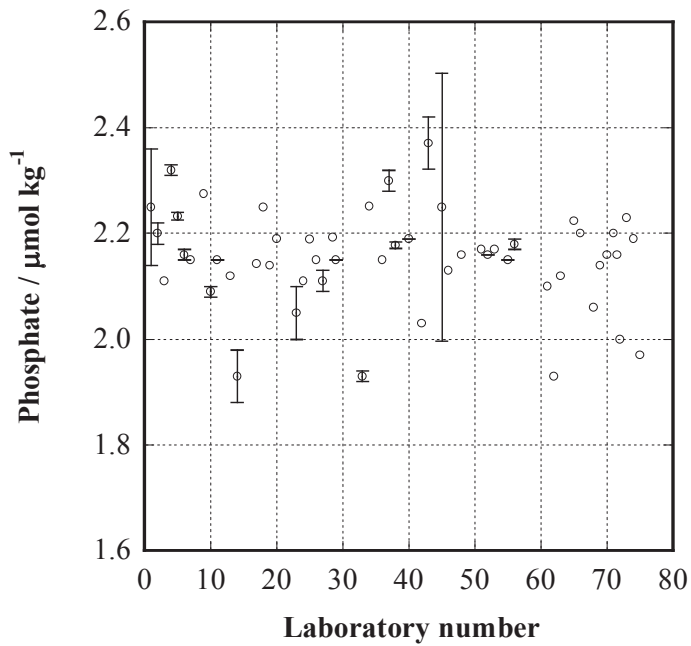


Figure A4-2 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #2 (lower panel)

## Sample 3 Phosphate

Consensus median:  $2.80 \pm 0.05 \mu\text{mol kg}^{-1}$

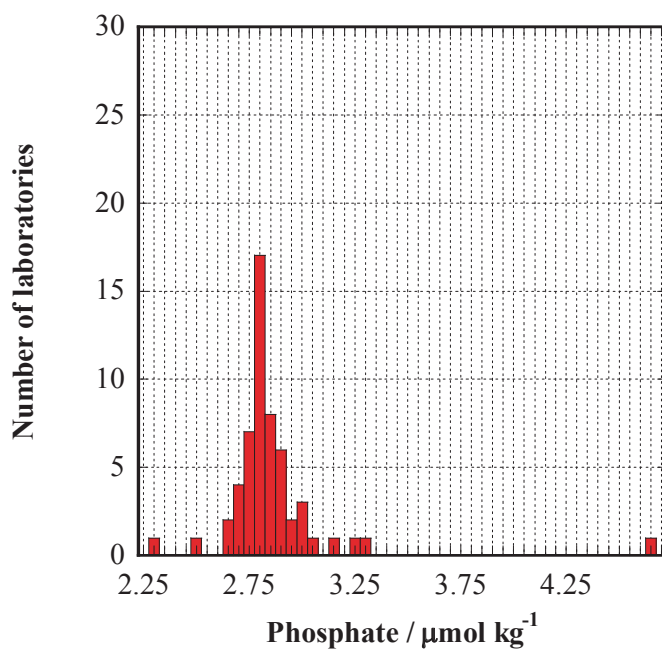
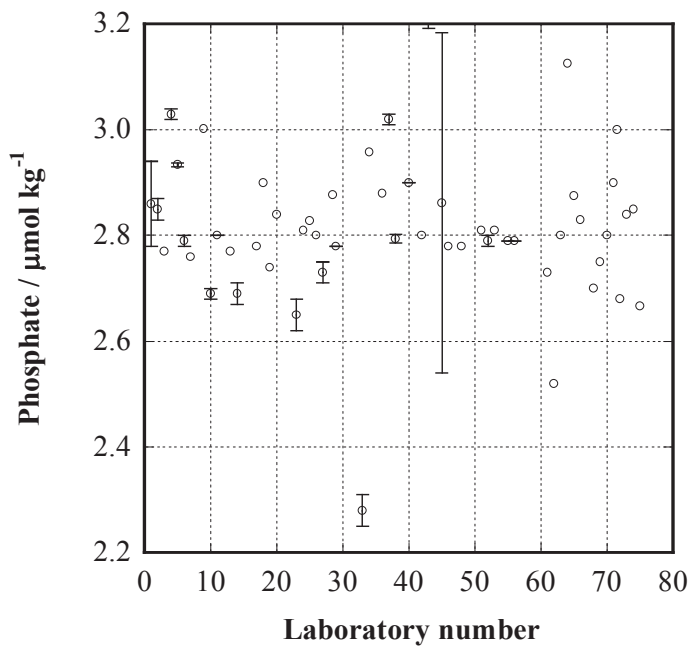


Figure A4-3 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #3 (lower panel)

## Sample 4 Phosphate

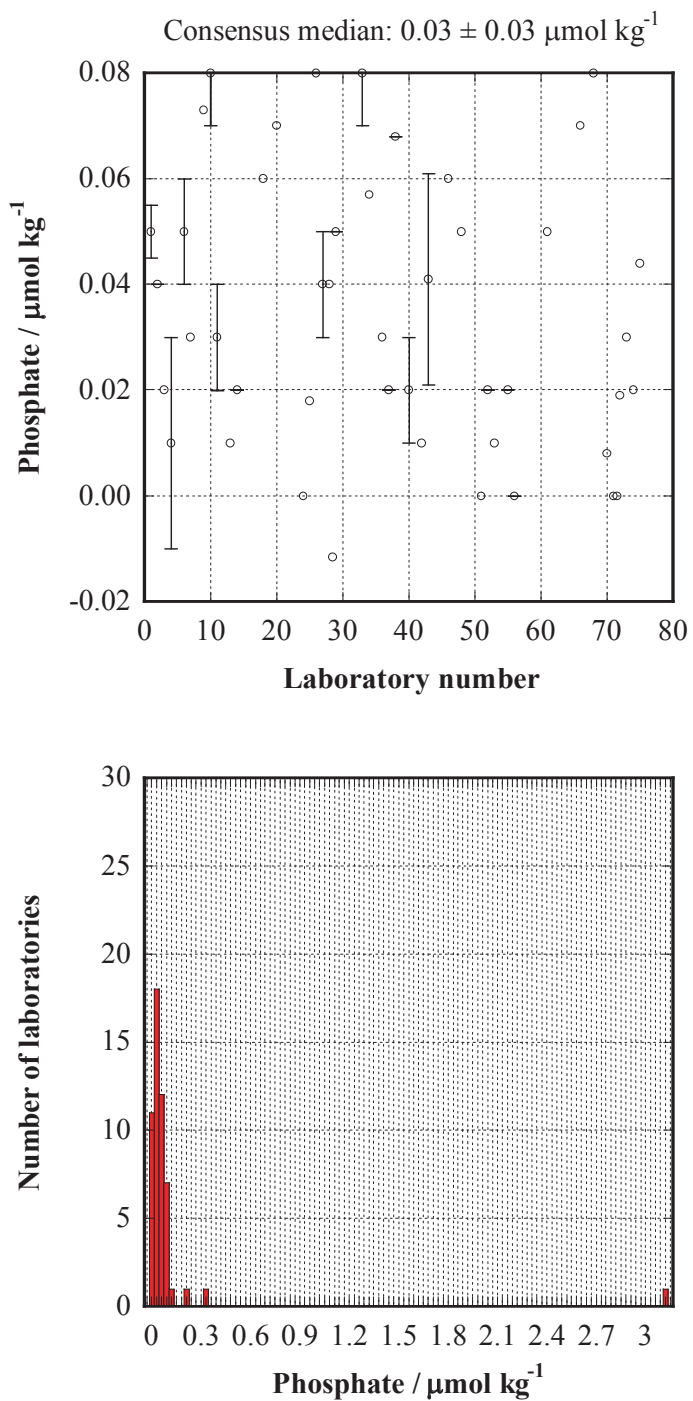


Figure A4-4 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #4 (lower panel)

## Sample 5 Phosphate

Consensus median:  $2.16 \pm 0.04 \mu\text{mol kg}^{-1}$

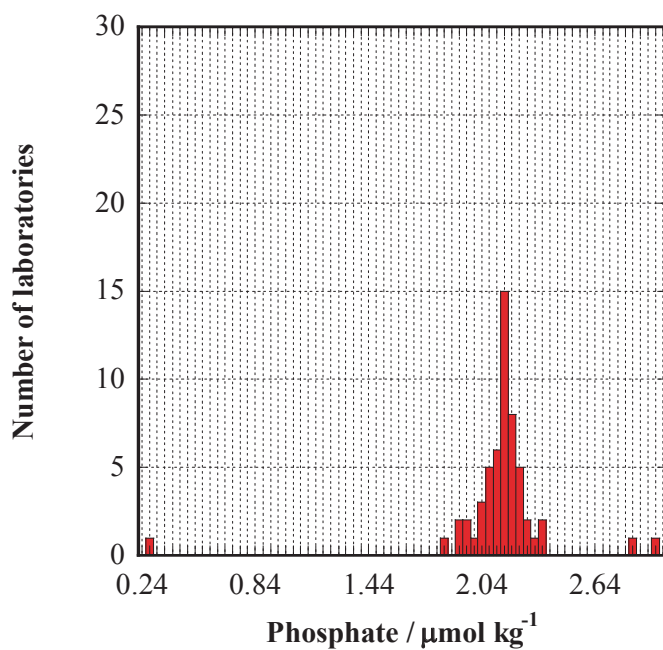
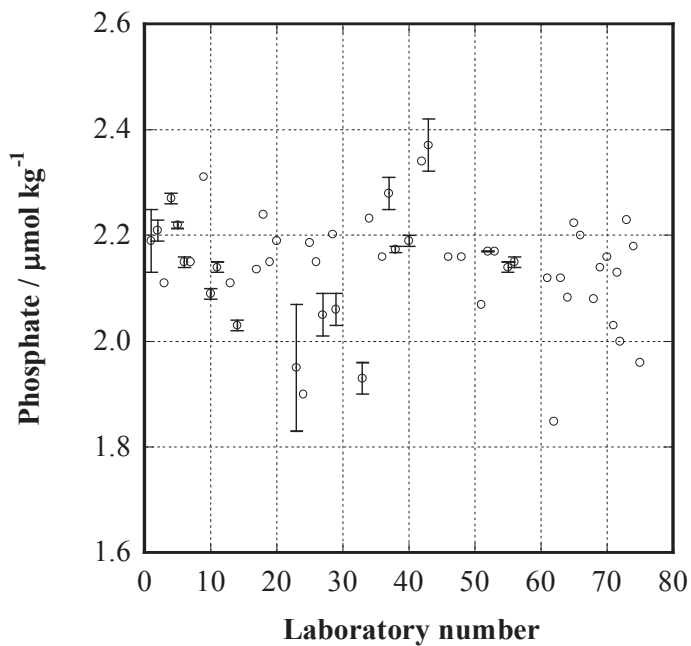


Figure A4-5 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #5 (lower panel)

## Sample 6 Phosphate

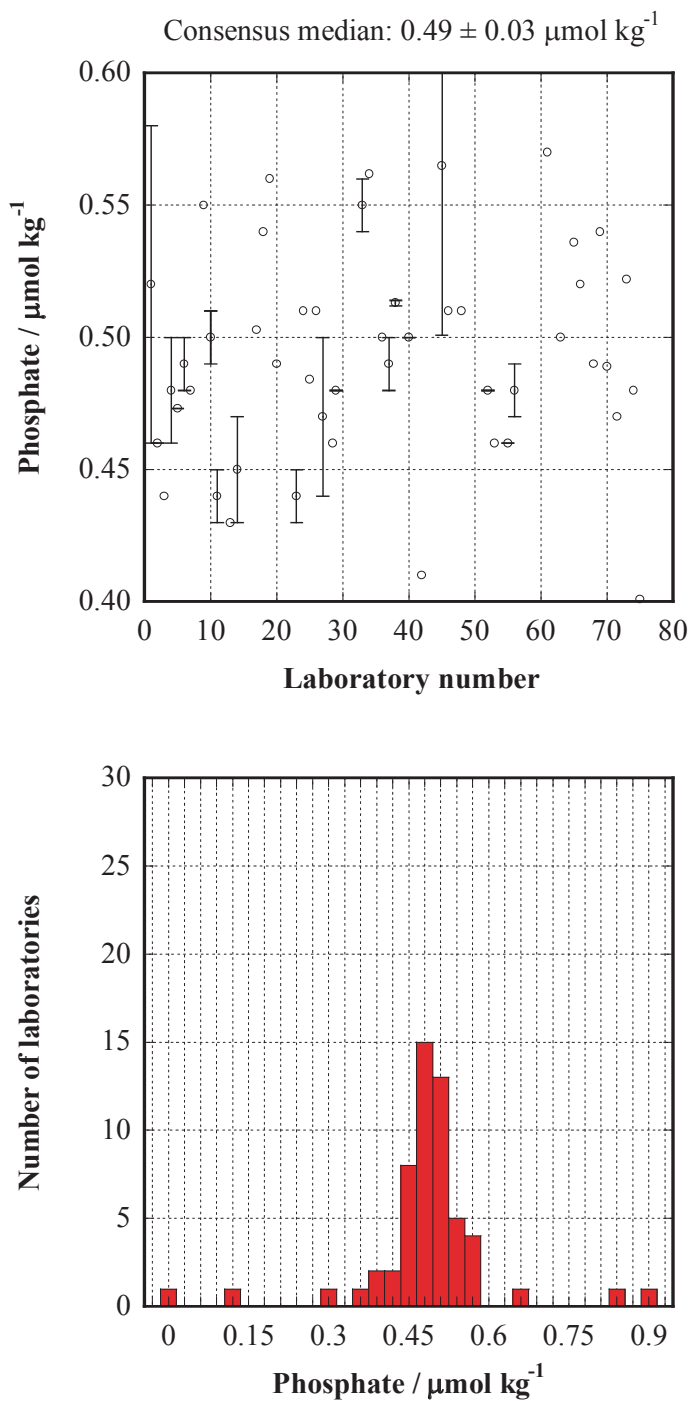


Figure A4-6 Phosphate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported phosphate concentration for sample #6 (lower panel)



## Sample 1 Silicate

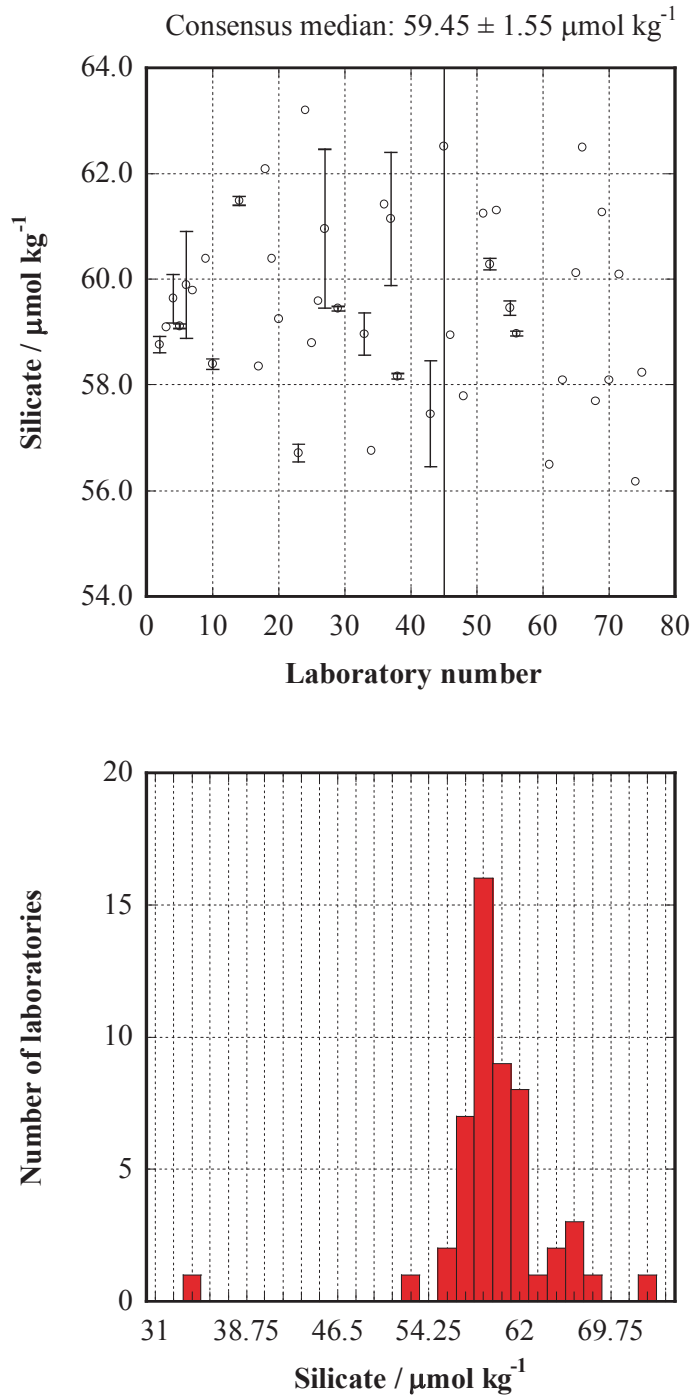


Figure A5-1 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #1 (lower panel)

## Sample 2 Silicate

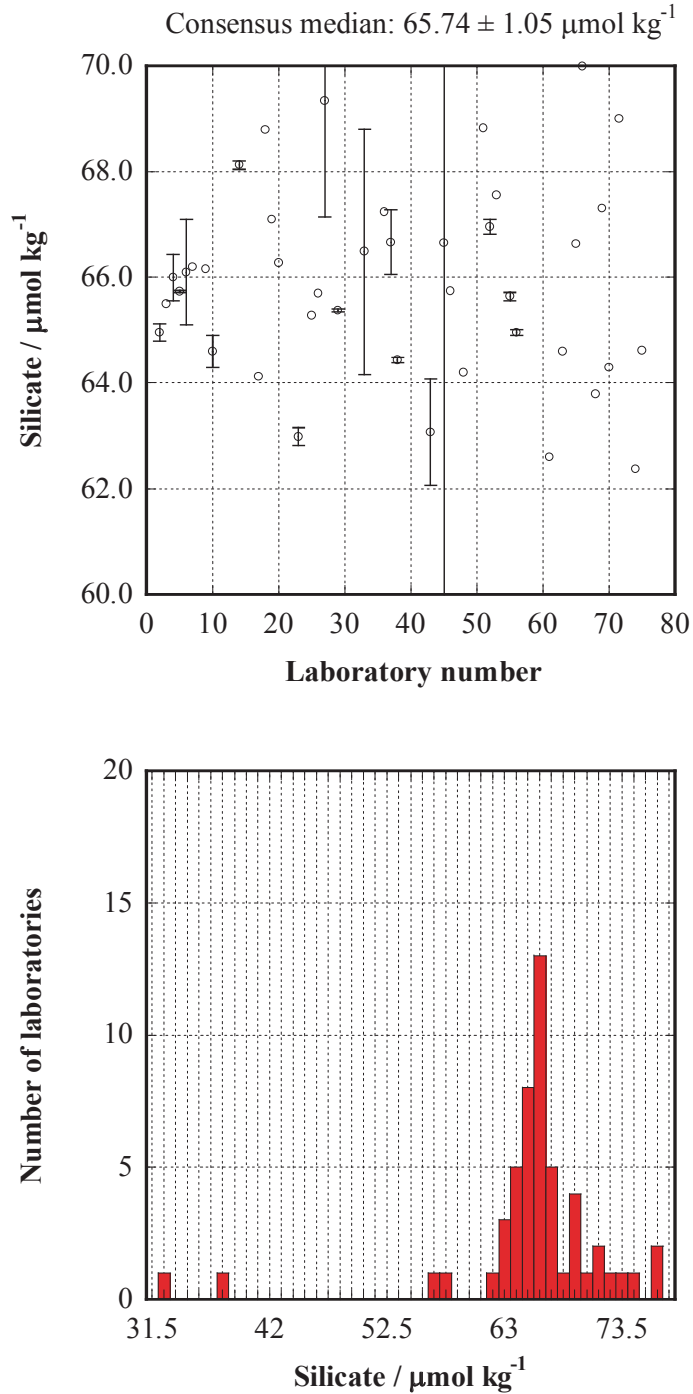


Figure A5-2 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #2 (lower panel)

### Sample 3 Silicate

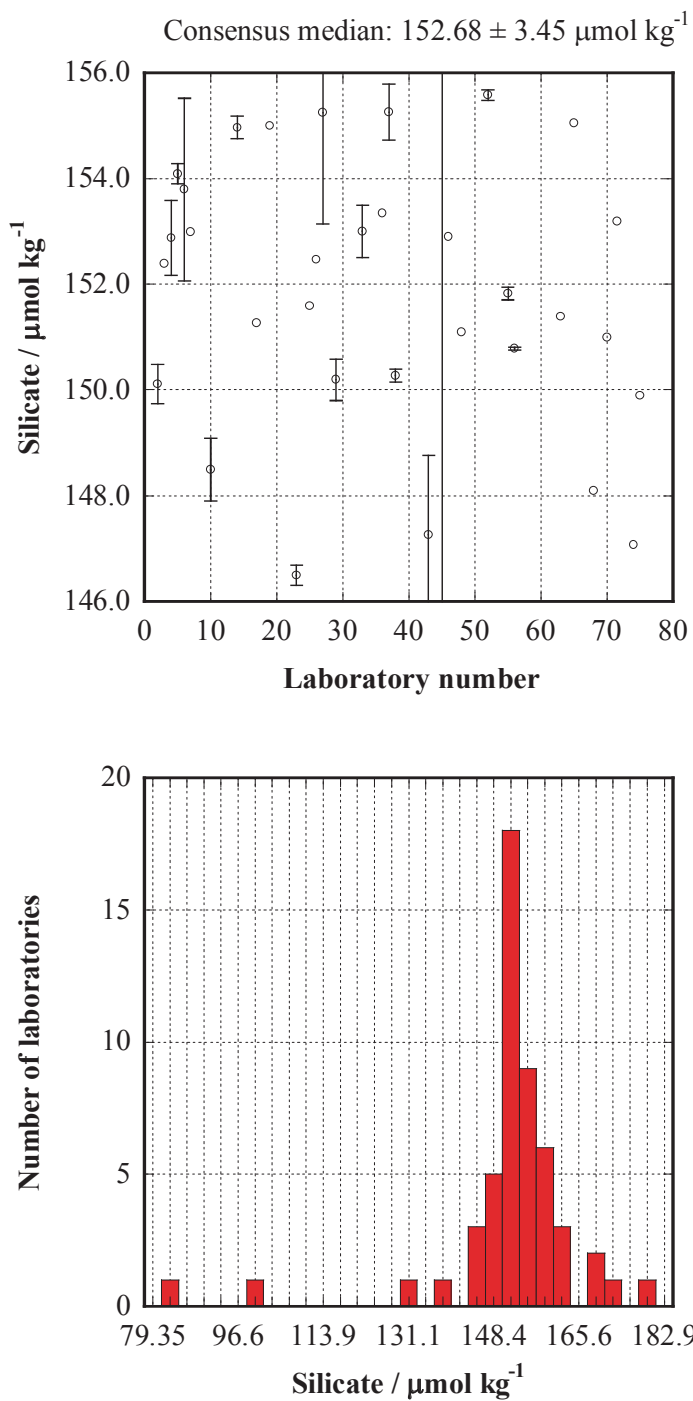


Figure A5-3 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration of sample #3 (lower panel)

## Sample 4 Silicate

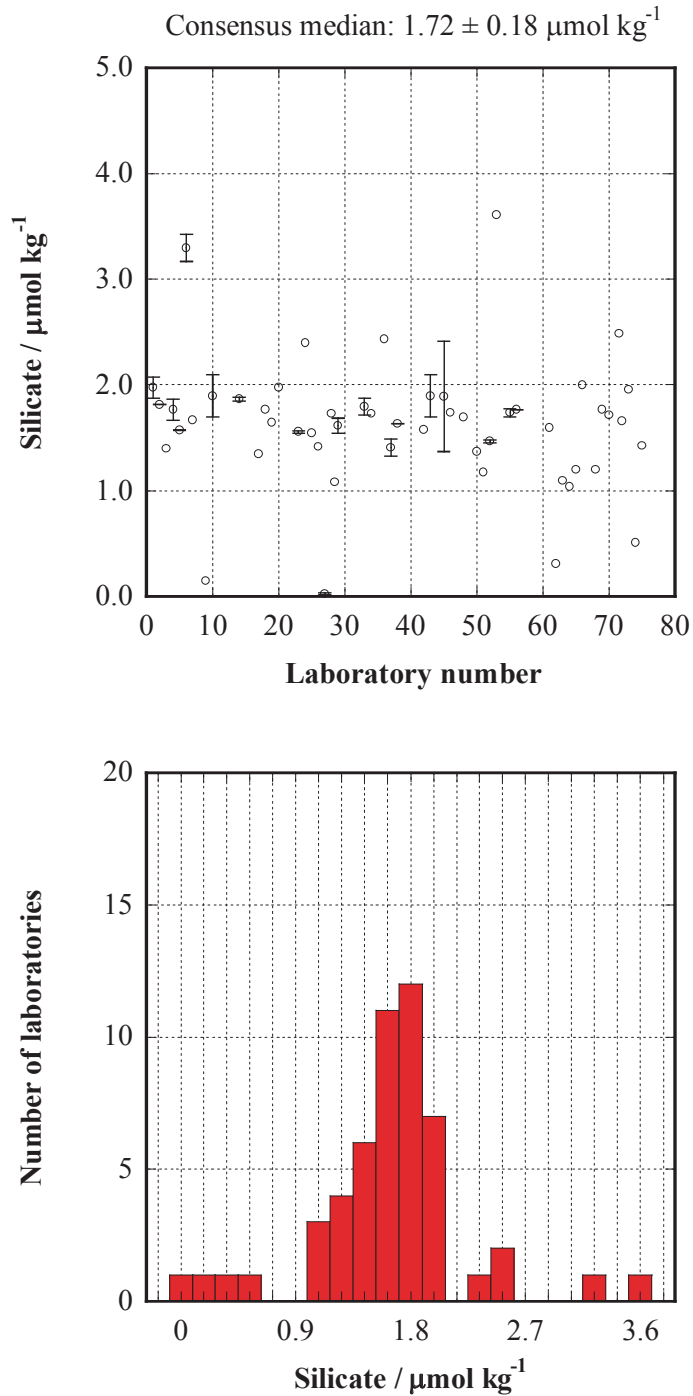


Figure A5-4 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration of sample #4 (lower panel)

## Sample 5 Silicate

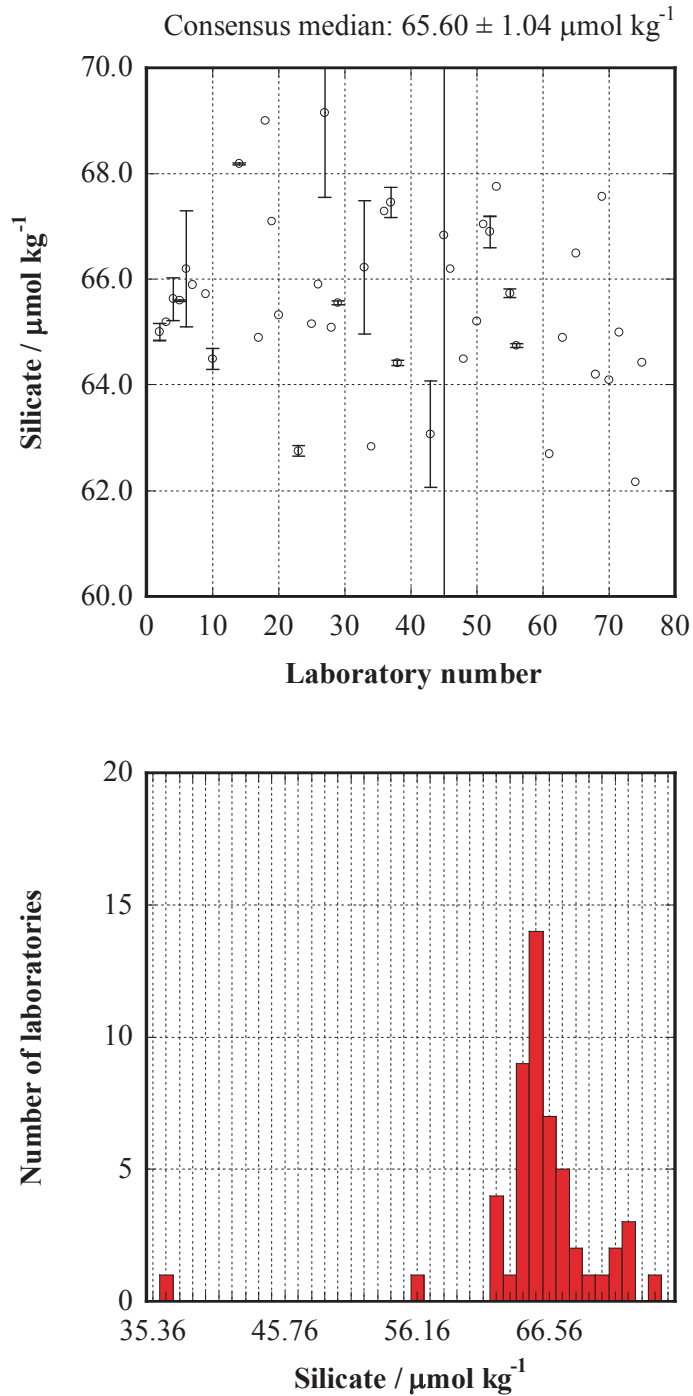


Figure A5-5 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #5 (lower panel)

## Sample 6 Silicate

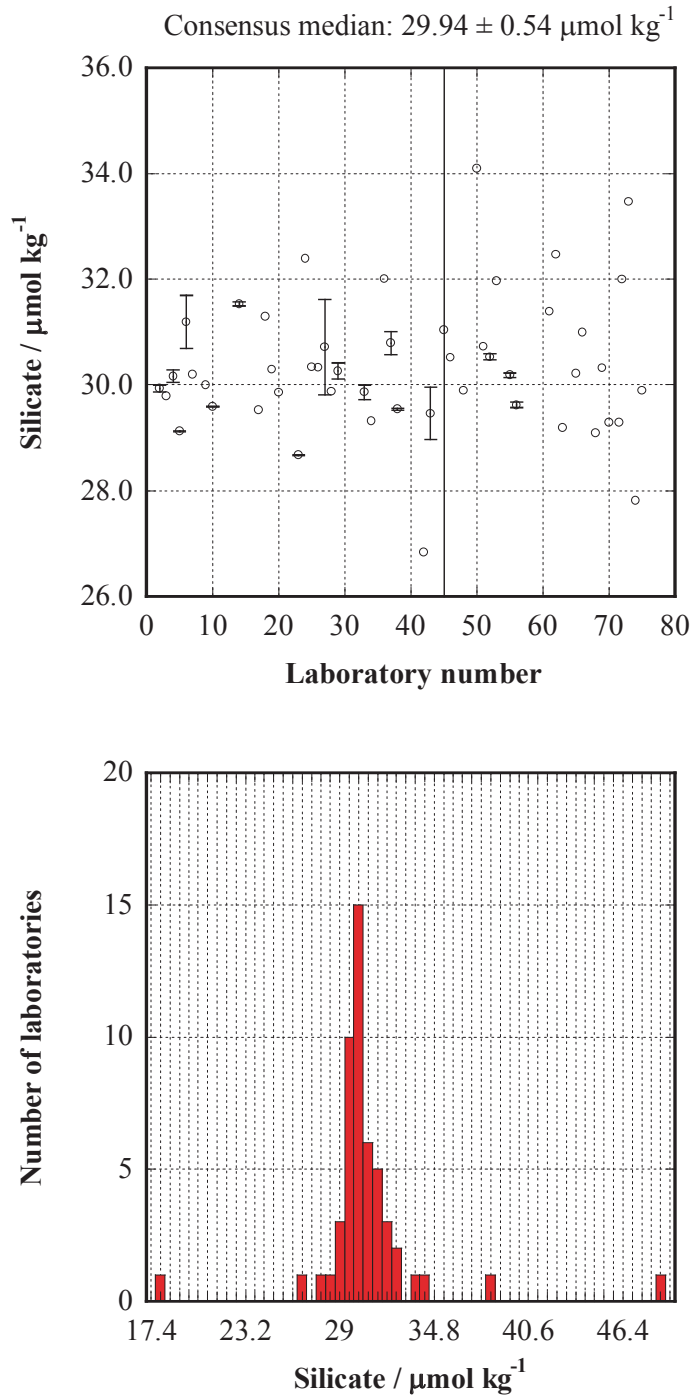


Figure A5-6 Silicate: concentrations *versus* laboratory number (upper panel) and frequency distribution of reported silicate concentration for sample #6 (lower panel)

## **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

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 led to the need to develop RMNSs is that absolutely pure chemicals are not available for the calibration of nutrient analyses, and that this is 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 a 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). LNSW; Low Nutrient Sea Water DIW; Deionised Water 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:

*Aranda*                                      Institute of Marine Research (IMR), Helsinki

*Hermann Wattenberg*                      Institut für Meereskunde, Kiel

*Skagerak*                                        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:

*Alkor*    Institut für Meereskunde, Kiel

*Okeanograf*                                      Institute of Marine Research, Leningrad

*Prof Otto Krammel*                            Institut für Meereskunde, Warnemünde

*Skagerak*                                        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 Methods<sup>2</sup>”, 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  $\mu\text{mol L}^{-1}$  for nitrate and 0.08–1.85  $\mu\text{mol L}^{-1}$  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 0–38  $\mu\text{mol kg}^{-1}$  for nitrate, 0–0.9  $\mu\text{mol kg}^{-1}$  for nitrite, 0–2.7  $\mu\text{mol kg}^{-1}$  for phosphate, and 0–136  $\mu\text{mol kg}^{-1}$  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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