The new era of nutrients measurements in seawater with RM/CRM and the new manual: The joint IOC-ICES Study Group on Nutrient Standards (SGONS) and recent progress

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Chairs of SGONS
27 Oct. 2010/ PICES 2010  S3
Talk outline

- The practical handbook, manuals
- Background and objective of SGONS
- What is **comparability** and how to obtain **comparability**?
- Present status of **comparability** of measurements of nutrients in seawater
- Work towards International Nutrients Scale System
- Homogeneity and stability of current RMNS
- Conclusions

※ToR: Terms of Reference

SGONS: Study Group on Nutrient Standards
The manual published in 1960: A practical handbook of seawater analysis

Standard methods of seawater analyses (Manuscript report series) J. D. H Strickland published in 1958
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Methods of Seawater Analysis
3rd 1999

Manuals
2008

Practical Guidelines for the Analysis of Seawater
2009

A manual of methods for the continuous flow determination of ammonia, nitrate-nitrite, phosphate and silicate in seawater (I.O.S. report) D. J Hydes 1984
WOCE manual
A Suggested Protocol for Continuous Flow Automated Analysis of Seawater Nutrients (Phosphate, Nitrate, Nitrite and Silicic Acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study
Louis I. Gordon, Joe C. Jennings, Jr., Andrew A. Ross, James M. Krest

4 November 1993
WOCE Hydrographic Program Office,
Methods Manual WHPO 91-1
DETERMINATION OF DISSOLVED NUTRIENTS (N, P, Si) IN SEAWATER WITH HIGH PRECISION AND INTER-COMPARABILITY USING GAS-SEGMENTED CONTINUOUS FLOW ANALYSERS

Abstract

Production of this manual is timely as it coincides with the development of reference materials for nutrients in seawater (RMNS). These RMNS solutions will be produced in sufficient quantities and be of sufficient quality that they will provide a basis for improving the consistency of nutrient measurements both within and between cruises.
Background and objective of IOC-ICES SGONS

※SGONS: Study Group on Nutrient Standards
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.

This strongly suggests a need to establish a strategy for obtaining high-quality oceanic nutrients data, based on the use of CRMs and well-characterized methodologies.

※CRMs : Certified Reference Materials
Summary. This document proposes a joint ICES-IOC study group to develop international standards for nutrients to establish comparability and traceability of nutrient data in the world oceans. This proposal was adopted last year.
Objective

Global comparability and traceability for measurements of nutrient in the global ocean through the development of certified reference materials and reference materials (CRMs/RMs).
The joint IOC-ICES Study Group on Nutrient Standards (SGONS)

“Towards developing an International Nutrients Scale System (INSS) using Reference Materials for nutrients in Seawater (RMNS) solutions”
Comparability? Traceability?

How to obtain comparability?
Comparability and traceability are defined as below.

Ilya Kuselman and Aleš Fajgelj, Fig. 3 of IUPAC/CITAC Guide: Selection and use of proficiency testing schemes for a limited number of participants—chemical analytical laboratories (IUPAC Technical Report), Pure Appl. Chem., Vol. 82, No. 5, pp. 1099–1135, 2010.
How to obtain comparability?

In the past: **manuals** and **adjust by offset**

*Inter-laboratory comparisons* – give idea of differences between labs.

**Synthesis** using mathematics methods and experience. Get apparent global **comparability** but does not have a firm foundation – accuracy is unknown.
How to obtain comparability?

Can now do scaling based on the RM
Theoretically correct way
Tested on cruises using RMs on CLIVAR lines
, SIO on CLIVAR - P6 in 2009, JMA on CLIVAR-
P9 in 2010.
JMA decided to use RM on CLIVAR cruises -
P13 in 2011, P3 in 2012 and all routine cruises
from this year.

※RM: Reference Material
CLIVAR: Climate Variability and Predictability
R/V: Research Vessel
SIO: Scripps Institution of Oceanography
JMA: Japan Meteorological Agency
How to obtain comparability?

In the past: manuals, I/C study and adjusted by offset
Present: scaling based on the RM

Future: International Nutrients Scale System

• **Comparability** with RM/CRM and a manual.
• **Traceability** and accuracy with CRM traceable to SI.

※**RM**: Reference Material
**CRM**: Certified Reference Material
**SI**: Le Systeme International d'Unites
Present status of comparability of measurements of nutrients in seawater
120 crossovers in the world ocean during WOCE and CLIVAR periods

※WOCE : World Ocean Circulation Experiment
※CLIVAR : Climate Variability and Predictability
Present status of comparability of nutrient data at P-03 and P-14 crossover point in the Pacific in 1980s-2000s

Ratio to reference cruises with RM at 120 crossovers

<table>
<thead>
<tr>
<th></th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>0.83±0.06</td>
<td>1.10±0.32</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.82±0.06</td>
<td>1.11±0.17</td>
</tr>
<tr>
<td>Silicate</td>
<td>0.83±0.09</td>
<td>1.20±0.04</td>
</tr>
</tbody>
</table>

※WOCE : World Ocean Circulation Experiment
CLIVAR : Climate Variability and Predictability
RM: Reference Material
Inter-laboratory comparison studies

Organized by MRI, Japan

2006 and 2008 RMNS I/C studies

55 laboratories in 15 countries

※MRI: Meteorological Research Institute
RMNS: Reference Materials for Nutrients in Seawater
I/C: Inter-comparison
2006 and 2008 Inter-laboratory Comparison Studies: participating laboratories

M. Aoyama et al., 2008: 2006 Inter-laboratory Comparison Study for Reference Material for Nutrients in Seawater. Technical Reports of the Meteorological Research Institute, No. 58

M. Aoyama et al., 2010: 2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater. Technical Reports of the Meteorological Research Institute, No. 60
Many laboratories have good internal comparability

Figure 7. **Comparability** of nitrate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.

![Figure 7](image)

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

![Figure 9](image)

Short summary of present status of nutrients data in the world

- Significant discrepancies between results from different laboratories both on land and on ship. (poor external comparability).
- Many laboratories have good internal comparability.

※MRI: Meteorological Research Institute
RMNS: Reference Materials for Nutrients in Seawater
I/C: Inter-comparison

M. Aoyama et al., 2010: 2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater. Technical Reports of the Meteorological Research Institute, No. 60
Work towards International Nutrients Scale System
2010 Paris meeting of SGONS

23-24 March 2010, UNESCO, Paris, France
32 participants, 11 countries
International Nutrients Scale System

Establish global **comparability** and **traceability** of sea water nutrient data from the worlds oceans through the development of appropriate certified reference materials (CRMs). NMIJ is working to certify our RM.
Coverage of International Nutrients Scale System, INSS, in sea water

The concentration ranges of determinands:
Nitrate (or Nitrate + Nitrite): 0 – 50 µmol kg\(^{-1}\)
Nitrite: 0 – 3 µmol kg\(^{-1}\)
Phosphate: 0 – 4 µmol kg\(^{-1}\)
Silicate: 0 – 250 µmol kg\(^{-1}\)
Ammonia: TBD
DOM: TBD

**Uncertainties** should be stated with each concentrations of nutrients

※DOM: Dissolved organic matter
Illustrating the effect of an International Nutrients Scale System

Illustrating the effect of an International Nutrients Scale System

How to obtain the comparability of nutrient measurements by INSS?

Use an agreed and internationally-distributed reference material with assigned nutrient values to:

1. determine a laboratory’s precision (internal comparability)
2. adjust data from multiple laboratories to a common calibration scale (external comparability).
Production of RMNS and homogeneity and stability of RMNS

Walk-in autoclave and 230 liters tank.
Now 350 liters.
2000 bottles of RMNS per a lot.
3500 bottles soon.

Clean room

RM in alminum bag
Homogeneity of RMNS

- Nitrate
- Phosphate
- Silicate

Year

Homogeneity / %
0.0 0.2 0.4 0.6 0.8 1.0 1.2

ICES I/C5
K
AH
BF
BG

Circled area: BF, BG
<table>
<thead>
<tr>
<th>Lot No.</th>
<th>Conc. µmol kg⁻¹</th>
<th>Time year</th>
<th>Initial Homogeneity</th>
<th>Estimated uncertainty due to long term stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH</td>
<td>35.54 ± 6.4</td>
<td>yes</td>
<td>0.44 ± 0.7</td>
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<tr>
<td>AV</td>
<td>33.88 ± 4.8</td>
<td>no</td>
<td>N.A.</td>
<td>0.2</td>
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<tr>
<td>AX</td>
<td>21.45 ± 4.8</td>
<td>yes</td>
<td>N.A.</td>
<td>0.2</td>
</tr>
<tr>
<td>BF</td>
<td>41.41 ± 1.9</td>
<td>yes</td>
<td>0.11 ± 0.20</td>
<td></td>
</tr>
</tbody>
</table>

**Stability of RMNS: Nitrate**

![Graph showing nitrate levels over time for different lots (AH, AV, AX, BF).](image)
<table>
<thead>
<tr>
<th>Lot</th>
<th>Conc. µmol kg⁻¹</th>
<th>Time year</th>
<th>ISO Guide</th>
<th>Stability</th>
<th>Initial Homogeneity</th>
<th>Estimated uncertainty due to long term stability (%)</th>
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</thead>
<tbody>
<tr>
<td>AH</td>
<td>2.13</td>
<td></td>
<td>35</td>
<td>yes</td>
<td>0.8</td>
<td>1.0</td>
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<tr>
<td>AV</td>
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<td></td>
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<td>yes</td>
<td>N.A.</td>
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<tr>
<td>AX</td>
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<td></td>
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<td>N.A.</td>
<td>0.4</td>
</tr>
<tr>
<td>BF</td>
<td>2.81</td>
<td></td>
<td></td>
<td>yes</td>
<td>0.21</td>
<td>0.38</td>
</tr>
</tbody>
</table>

**Stability of RMNS: Phosphate**

![Graph showing the stability of phosphate over the years](chart.png)
Stability of RMNS: Silicate

<table>
<thead>
<tr>
<th>Lot No.</th>
<th>Conc. µmol kg⁻¹</th>
<th>Time year</th>
<th>Initial Homogeneity</th>
<th>Estimated uncertainty due to long term stability %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH</td>
<td>132.6</td>
<td>yes</td>
<td>0.15</td>
<td>0.6</td>
</tr>
<tr>
<td>AV</td>
<td>154.4</td>
<td>yes</td>
<td>N.A.</td>
<td>0.1</td>
</tr>
<tr>
<td>AX</td>
<td>58.21</td>
<td>yes</td>
<td>N.A.</td>
<td>0.2</td>
</tr>
<tr>
<td>BF</td>
<td>150.58</td>
<td>yes</td>
<td>0.08</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Graph showing the stability of Silicate over time from 2003 to 2010, with markers for AH, AV, AX, and BF.
Conclusions
Conclusions-1

• Use of RMNS provides measures of precision and accuracy so we can proceed to studies of change in deep water related to climate changes.

※RMNS: Reference Materials for Nutrients in Seawater
Conclusions-2

• A key aim of the joint IOC-ICES Study Group on Nutrient Standards (SGONS) is to establish an “International Nutrients Scale System (INSS)” appropriate for improving the comparability and traceability of nutrient data in the world's oceans.

• SGONS published “Determination of nutrients in seawater with high precision and inter-comparability using gas-segmented continuous flow analysers”. It discusses how RMNS solutions can be used to “track” the performance of a system during a cruise and between cruises.

• Adoption of these standards will facilitate understanding of changes in ocean chemistry and biology by making data more readily comparable across laboratories.
Comparability of nutrients in the world's ocean

INSS international workshop 10-12 Feb. 2009, Paris

Editor in Chief
Michio Aoyama
Thank you for your attention