United Nations Educational, Scientific and Cultural Organization

Organisation des Nations Unies pour l'éducation la science et la culture

Organización de las Naciones Unidas para la Educación la Ciencia y la Cultura

Организация Объединенных Наций по вопросам образования науки и культуры

Intergovernmental Oceanographic Commission

Commission océanographique intergouvernementale

Comisión Oceanográfica Intergubernamental

Межправительственная океанографическая комиссия

1960-2010

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

Michio Aoyama, Meteorological Res. Inst, Japan and

David Hydes, National Oceanography Center, UK

Chairs of SGONS

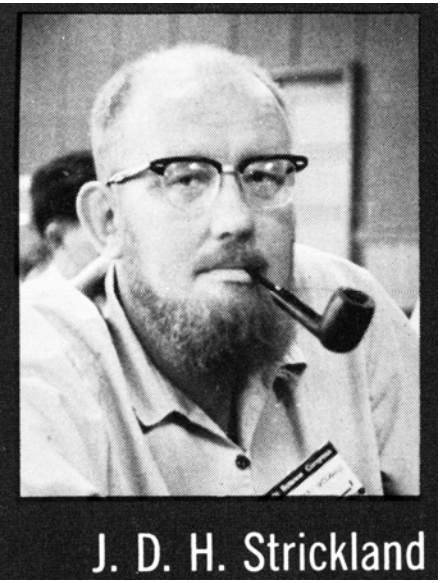
27 Oct. 2010/ PICES 2010 S3

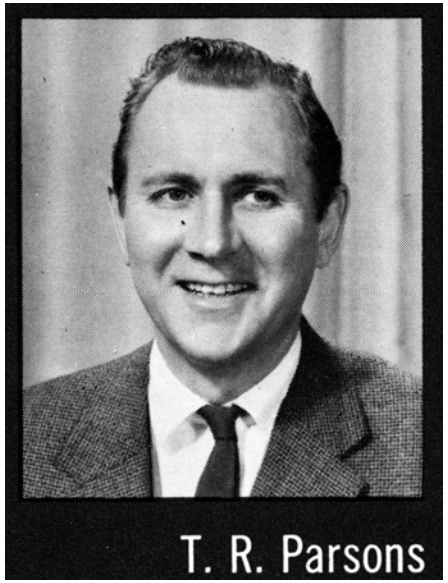
Talk outline

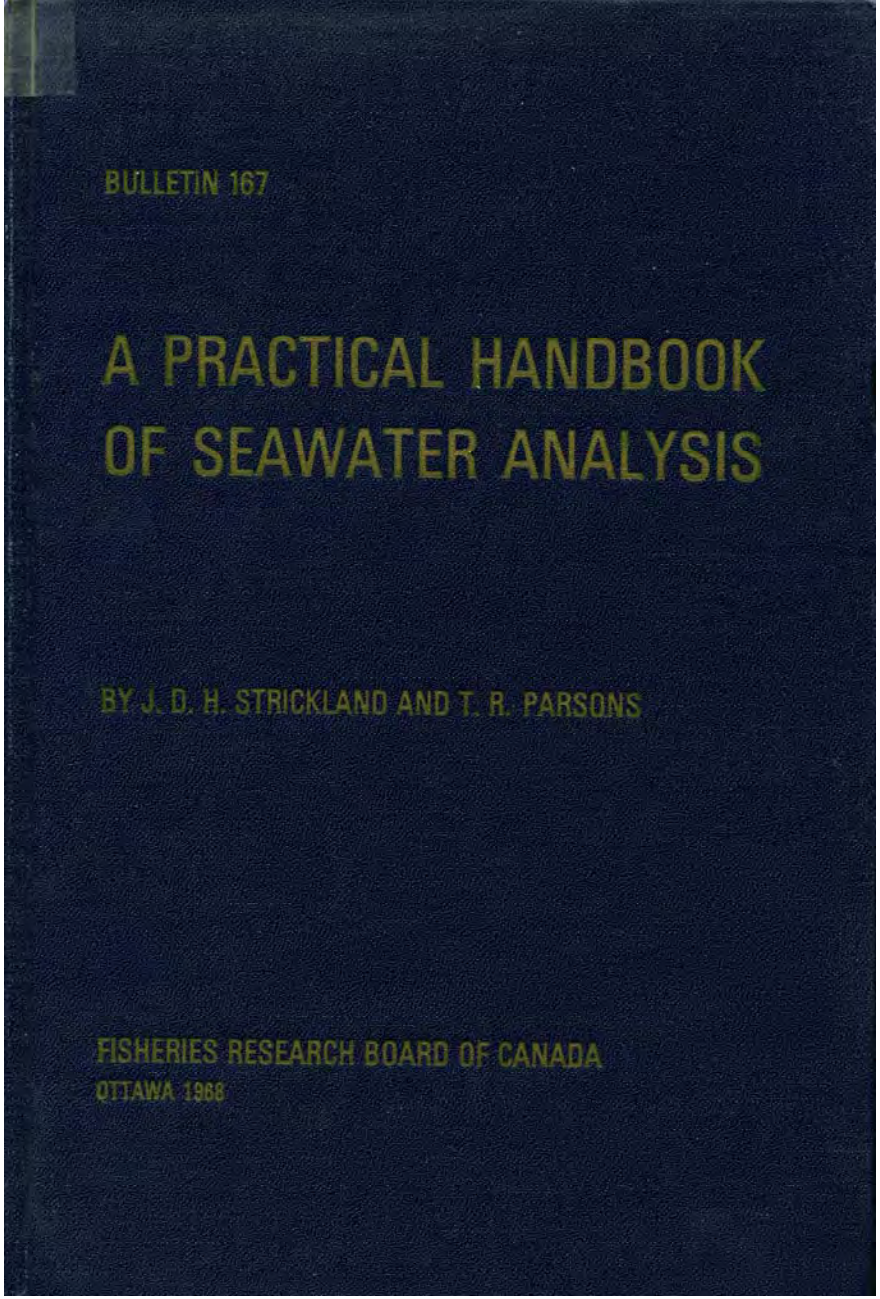
- The practical handbook, manuals
- Background and objective of SGONS
- What is **comparability** and how to obtain **comparability**?
- Present status of **comparability** of measurements of nutrients in seawater
- Work towards International Nutrients Scale System
- Homogeneity and stability of current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

※**ToR** : Terms of Reference
SGONS: Study Group on Nutrient Standards

The manual published in 1960:
A practical handbook of seawater analysis


J. D. H. Strickland


T. R. Parsons



Standard methods of seawater analyses (Manuscript report series) J. D. H Strickland published in 1958

Contents

PREFACE, 1

ACKNOWLEDGMENTS, 3

NOTE ON STATISTICAL LIMITS, 5

NOTES ON APPARATUS, 7

PART I. SALINITY, DISSOLVED OXYGEN, CARBONATE AND SULPHIDE, 11
- I.1. Determination of salinity by titration (high precision), 11
- I.2. Determination of salinity by titration (low precision), 17
- I.3. Determination of dissolved oxygen, 21
- I.4. Determination of carbonate, bicarbonate, and free carbon dioxide from *p*H and alkalinity measurements, 27
  - I.4.I. Determination of experimental quantities, 29
  - I.4.II. Calculation and use of tables, 33
- I.5. Direct determination of total carbon dioxide, 35
- I.6. Determination of sulphide, 41

PART II. INORGANIC MICRONUTRIENTS IN SEA WATER, 45
- II.1. Introductory remarks on a differentiation of the various forms of phosphorus, 45
- II.2. Determination of phosphorus, 49
  - II.2.I. Determination of reactive phosphorus, 51
  - II.2.II. Determination of reactive phosphorus (low levels), 53
- II.3. Determination of total phosphorus, 57
- II.4. Determination of inorganic polyphosphate, 63
- II.5. Determination of reactive silicate, 65
- II.6. Determination of reactive nitrate, 71
- II.7. Determination of reactive nitrite, 77
- II.8. Determination of ammonia plus amino acids, 81
- II.9. Determination of ammonia, 87
- II.10. Determination of hydroxylamine, 93
- II.11. Determination of reactive iron, 97
  - II.11.I. Determination of particulate iron, 99
  - II.11.II. Determination of soluble iron, 105
- II.12. Determination of manganese, 109
- II.13. Determination of copper, 115
- II.14. Automated nutrient analysis, 119
  - II.14.I. Description of apparatus, 119
  - II.14.II. Nutrient analysis, 125
    - II.14.II.1. Nitrate, 125
    - II.14.II.2. Nitrite, 129

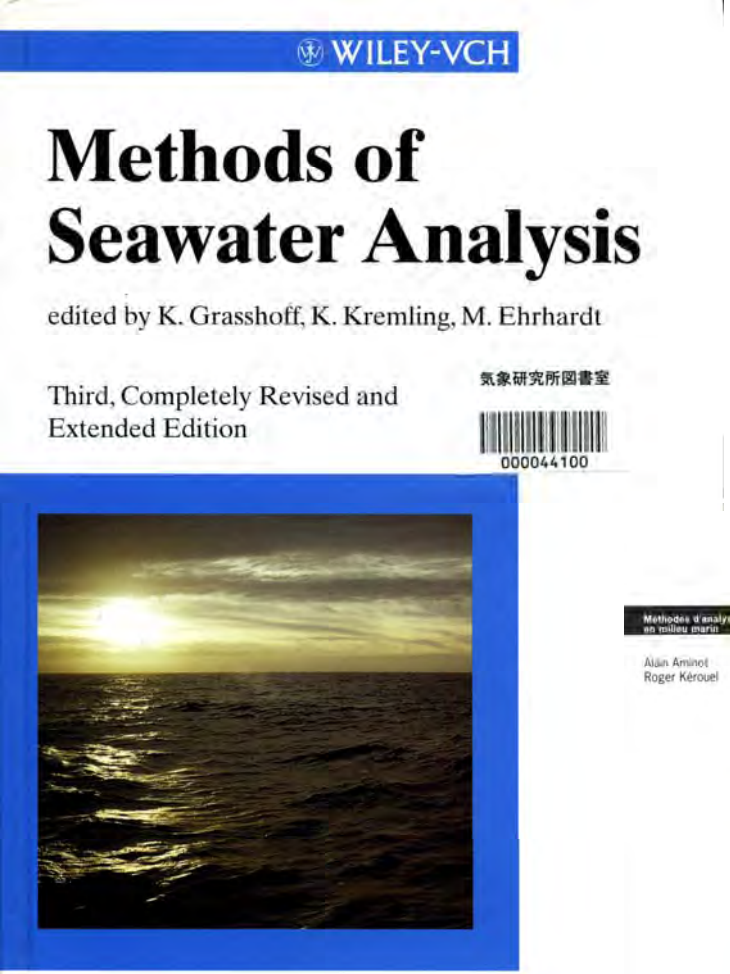
Contents — Continued

- II.14.II.3. Ammonia (plus amino acids), 131
- II.14.II.4. Phosphate, 135
- II.14.II.5. Silicate, 137

PART III. DETERMINATION OF SOLUBLE ORGANIC MATTER, 139
- III.1. Determination of monophosphate esters, 139
- III.2. Determination of soluble organic phosphorus by ultraviolet light oxidation, 141
- III.3. Determination of soluble organic nitrogen, 143
  - III.3.I. Kjeldahl digestion, 143
  - III.3.II. Ultraviolet light oxidation, 149
- III.4. Determination of soluble organic carbon, 153
- III.5. Determination of cyanocobalamine (vitamin B_{12}), 159
- III.6. Determination of biotin, 165
- III.7. Determination of thiamine (vitamin B_1), 169
- III.8. Determination of carbohydrate, 173

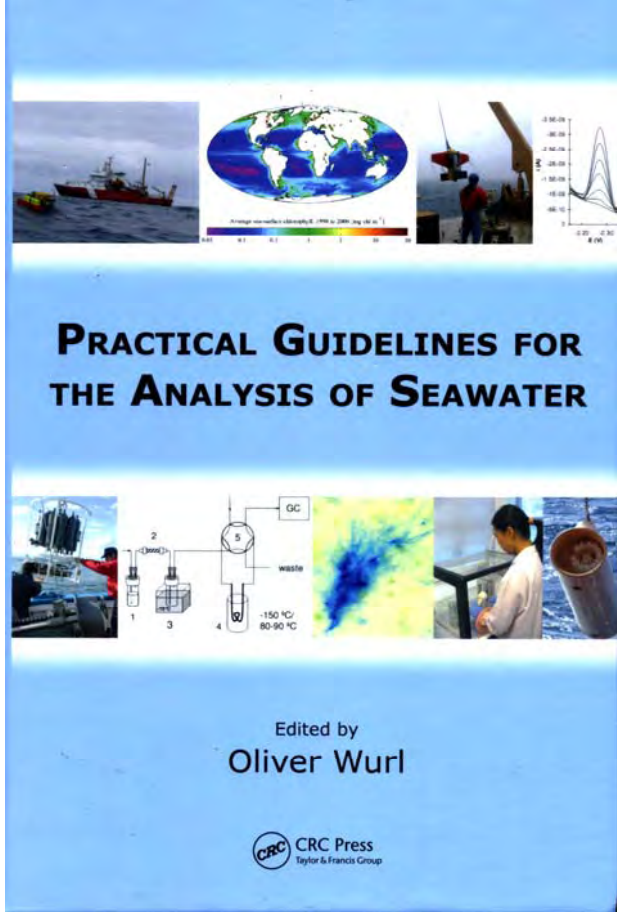
PART IV. DETERMINATION OF PARTICULATE MATERIALS, 175
- IV.1. Introductory remarks on different methods for determining particulate materials in aquatic environments, 175
- IV.2. A separation of microscopic particles from sea water, 177
  - IV.2.I. Determination of the weight of microscopic materials in sea water, 181
- IV.3. Pigment analysis, 185
  - IV.3.I. Spectrophotometric determination of chlorophylls and total carotenoids, 185
    Addendum to IV.3.I. Spectrophotometric determination of phaeo-pigments, 193
  - IV.3.II. SCOR/UNESCO procedure for chlorophylls, 195
  - IV.3.III. Determination of chlorophyll *c*, 197
  - IV.3.IV. Fluorometric determination of chlorophylls, 201
    Addendum to IV.3.IV. Fluorometric determination of phaeo-pigments, 203
  - IV.3.V. Automated estimation of chlorophyll pigments by fluorescence, 205
- IV.4. Determination of particulate carbon, 207
  - IV.4.I. Wet oxidation with dichromate, 207
  - IV.4.II. Combustion in oxygen (high levels), 213
  - IV.4.III. Combustion in oxygen (low levels), 215
- IV.5. Determination of particulate phosphorus, 219
- IV.6. Determination of particulate nitrogen, 221
  - IV.6.I. Combustion method (high levels), 221
  - IV.6.II. Kjeldahl method with ninhydrin finish (low levels), 223
- IV.7. Determination of particulate lipid, 227

Manuals



3rd 1999

2008



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

OSU Coll. of Oc. Descriptive. Chem. Oc. Grp. Tech. Rpt. 93-1

WOCE Hydrographic Program Office,

Methods Manual WHPO 91-1

GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines

IOCCP Report No. 14

ICPO Publication Series No. 134

Version 1, 2010

DETERMINATION OF DISSOLVED NUTRIENTS (N, P, SI) IN SEAWATER WITH HIGH PRECISION AND INTER-COMPARABILITY USING GAS-SEGMENTED CONTINUOUS FLOW ANALYSERS

D. J. Hydes, M. Aoyama, A. Aminot, K. Bakker, S. Becker, S. Coverly, A. Daniel, A. G. Dickson, O. Grosso, R. Kerouel, J. van Ooijen, K. Sato, T. Tanhua, E. M. S. Woodward, J. Z. Zhang

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.

RMNS approach

Background and objective of IOC-ICES SGONS

※**SGONS**: Study Group on Nutrient Standards

Background

IPCC 2007 WG1 Chapter 5

5.4.4 Nutrients

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

IOC/INF-1260
Paris, 11 May 2009
English only*

INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION
(of UNESCO)

INFORMATION DOCUMENT

A JOINT ICES-IOC
STUDY GROUP ON NUTRIENT STANDARDS (SGONS)

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.

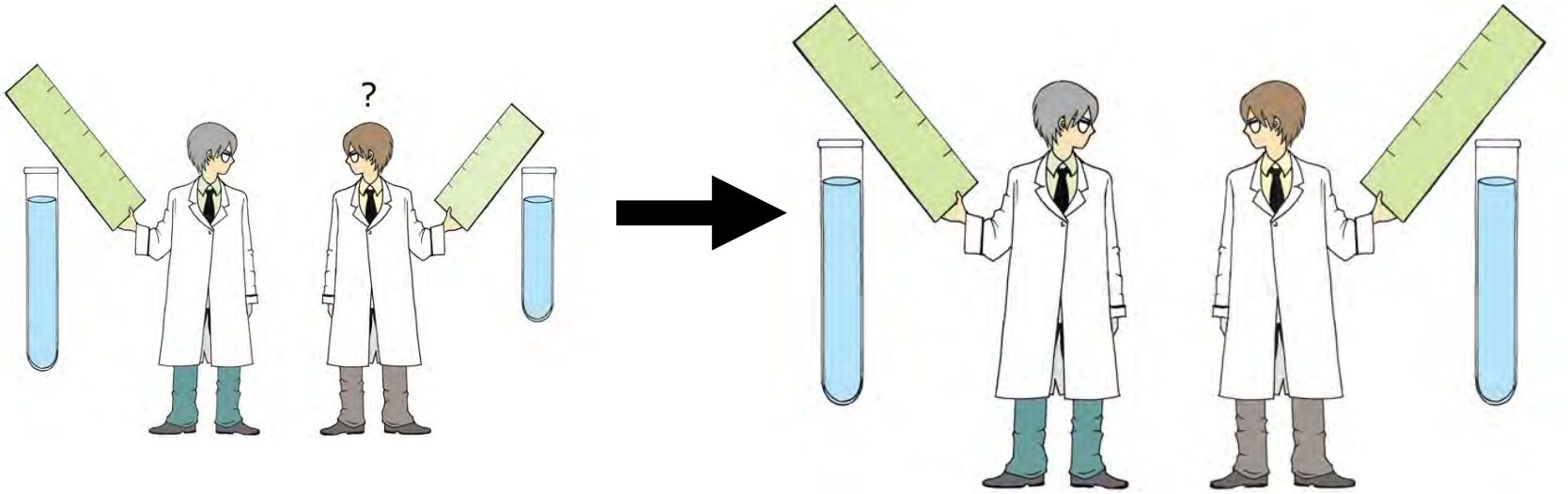
This proposal was adopted last year.

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)

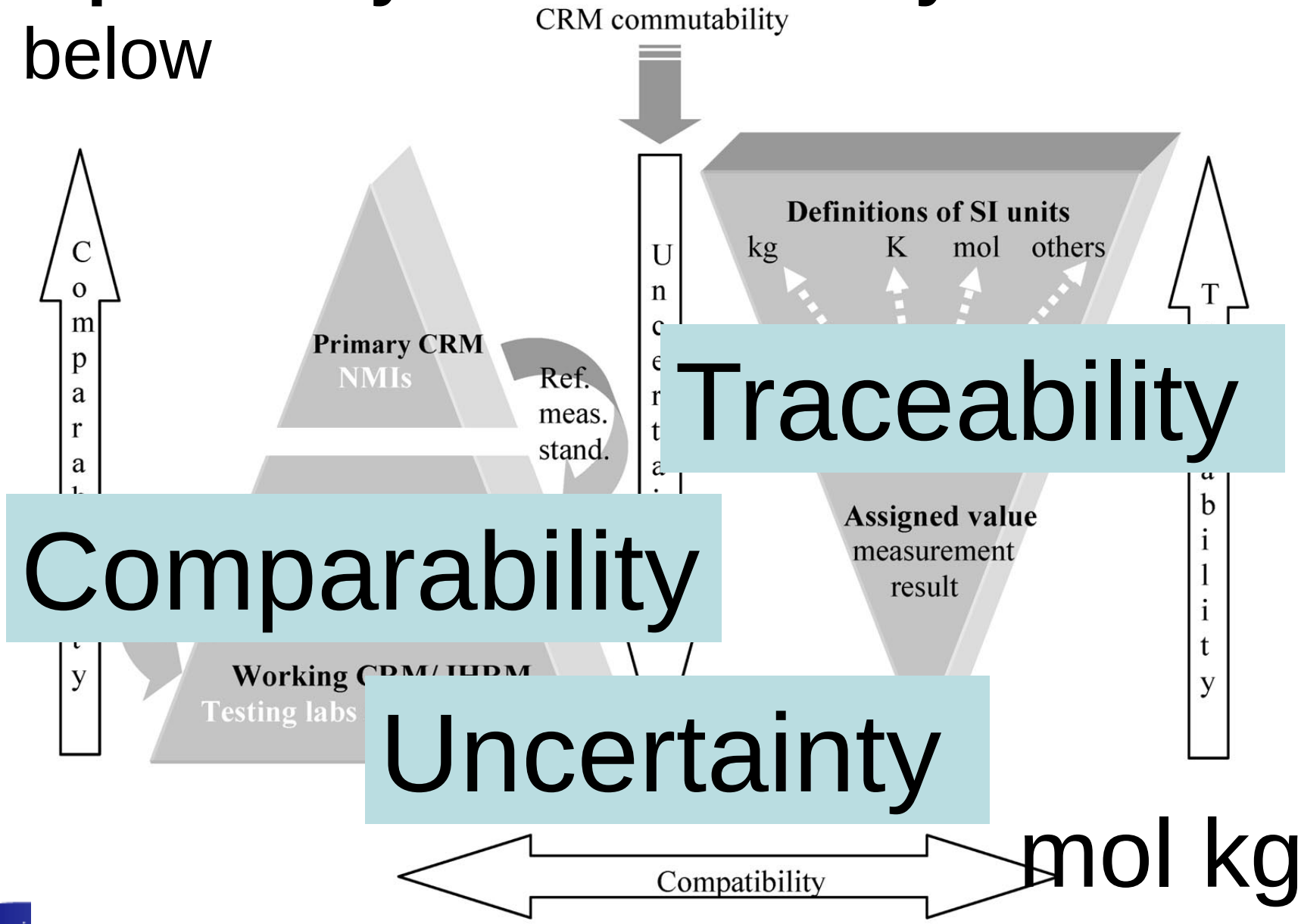
"Towards developing an International Nutrients Scale System (INSS) using Reference Materials for nutrients in Seawater (RMNS) solutions"



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

R/V Mirai cruises in 2003, 2005, 2007 and 2009. , 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

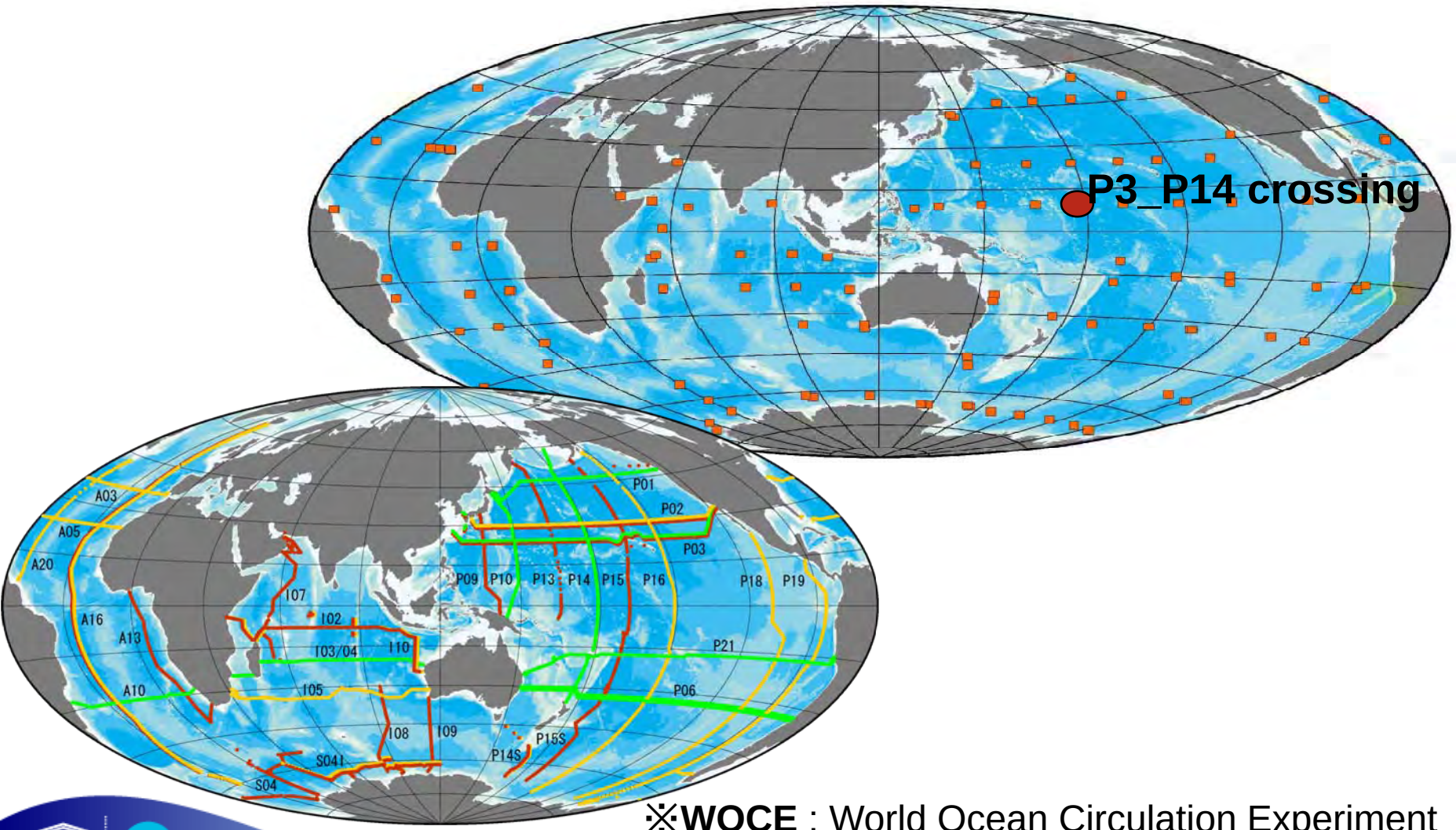
Future: International Nutrients Scale System

- **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

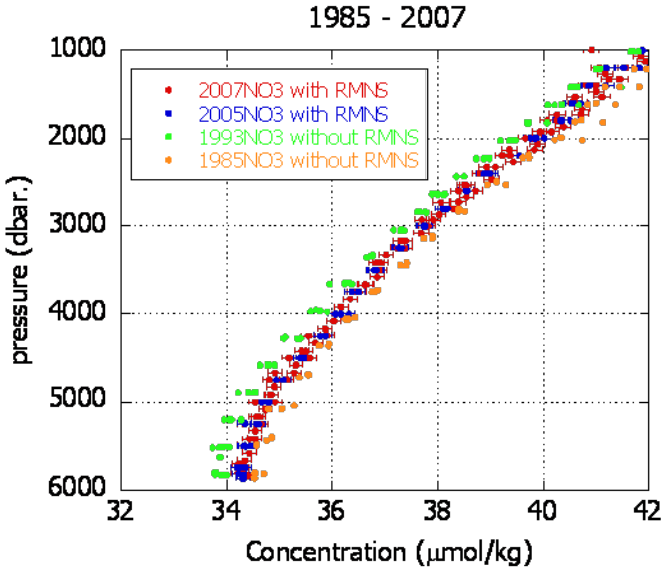
Present status of comparability of measurements of nutrients in seawater

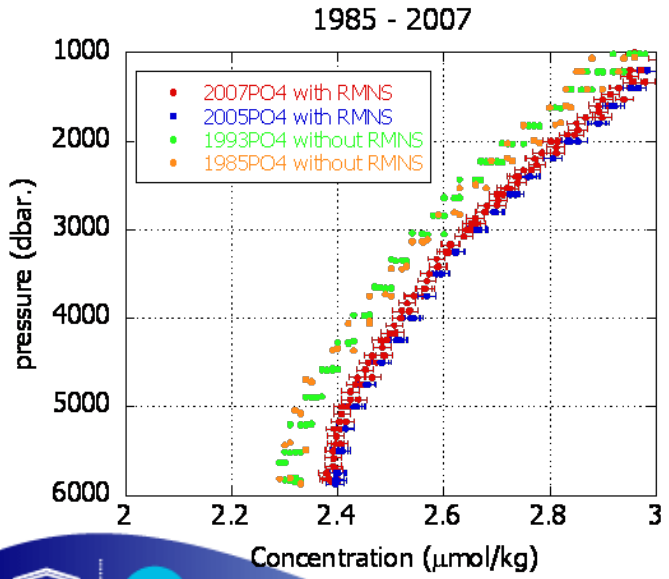
120 crossovers in the world ocean during WOCE and CLIVAR periods

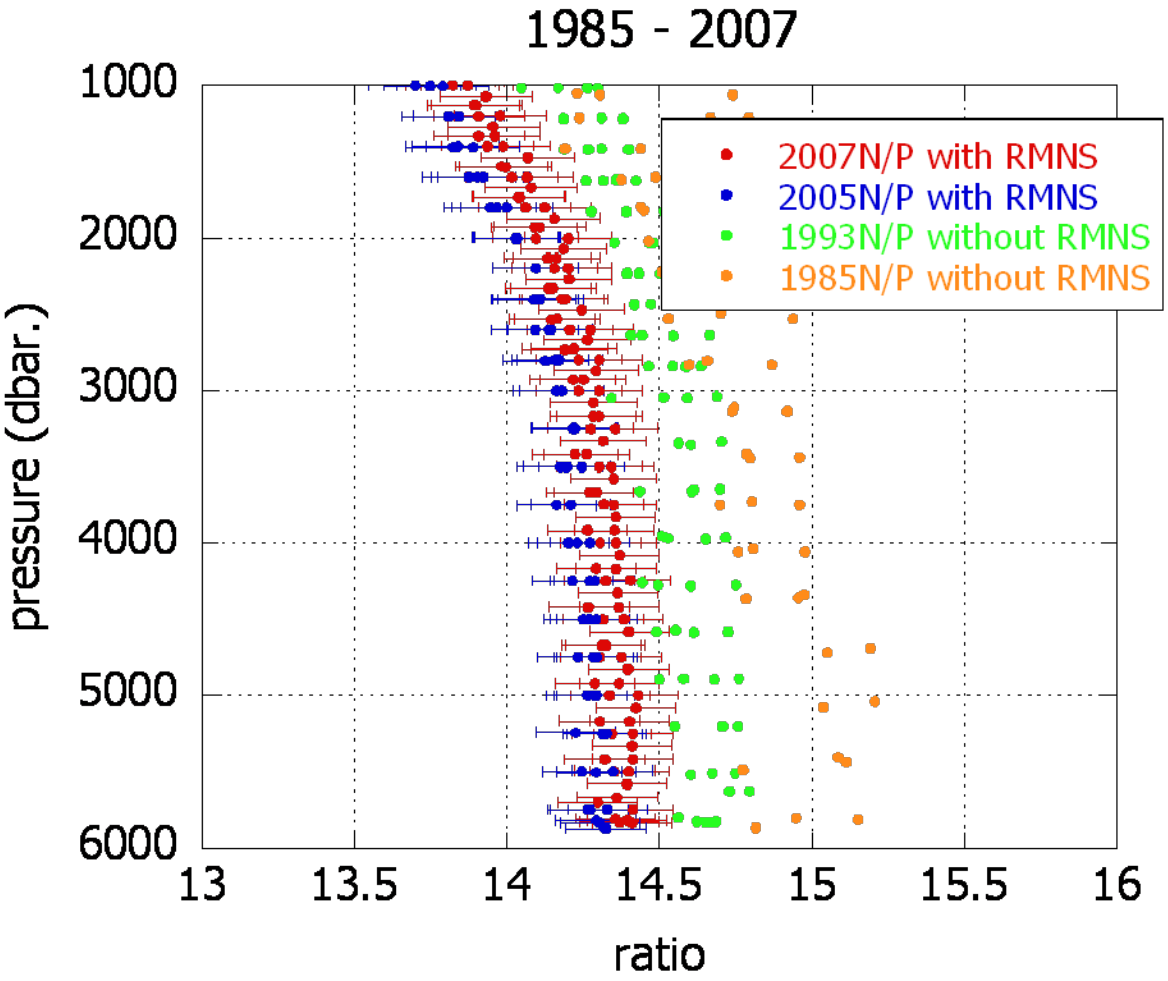


※**WOCE** : World Ocean Circulation Experiment
CLIVAR : Climate Variability and Predictability

Present status of comparability of nutrient data at P-03 and P-14 crossover point in the Pacific in 1980s-2000s







Aoyama, M. & Co-Authors (2010). "A Joint ICES-IOC Study Group On Nutrient Standards" in Proceedings of OceanObs'09: Sustained Ocean Observations and Information for Society (Annex), Venice, Italy, 21-25 September 2009, Hall, J., Harrison, D.E. & Stammer, D., Eds., ESA Publication WPP-306.

Ratio to reference cruises with RM at 120 crossovers

	Min	Max
Nitrate	0.83±0.06	1.10±0.32
Phosphate	0.82±0.06	1.11±0.17
Silicate	0.83±0.09	1.20±0.04

※**WOCE** : World Ocean Circulation Experiment
CLIVAR : Climate Variability and Predictability
RM: Reference Material

Inter-laboratory comparison studies

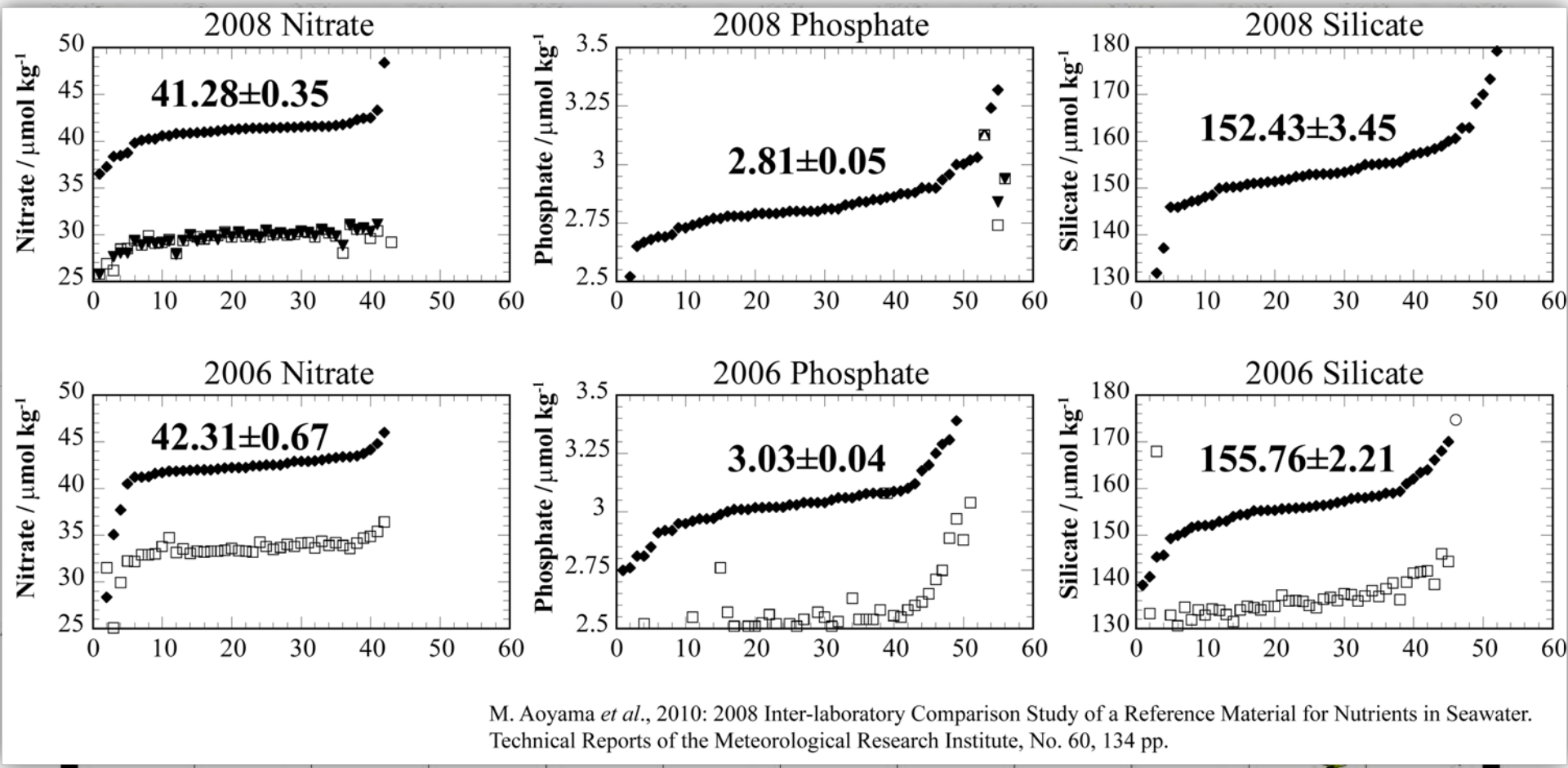
Organized by MRI, Japan

2006 and 2008 RMNS I/C studies

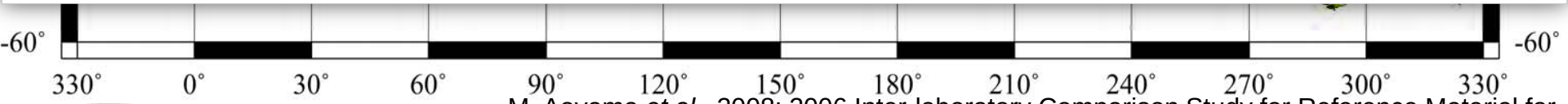
55 laboratories in 15 countries

※**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*., 2010: 2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater. Technical Reports of the Meteorological Research Institute, No. 60, 134 pp.



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

IOC

Many laboratories have good internal comparability

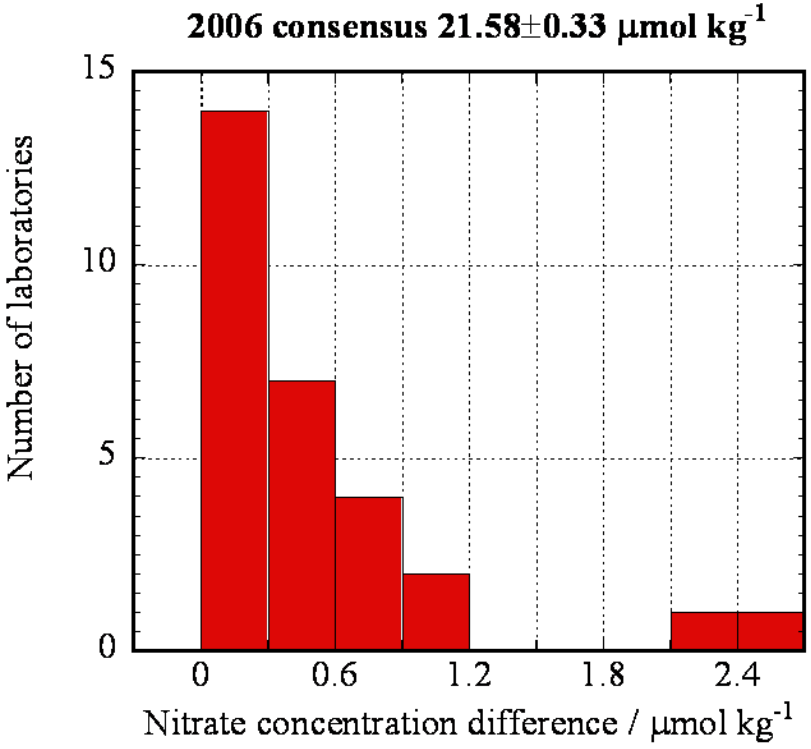


Figure 7. **Comparability** of nitrate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.

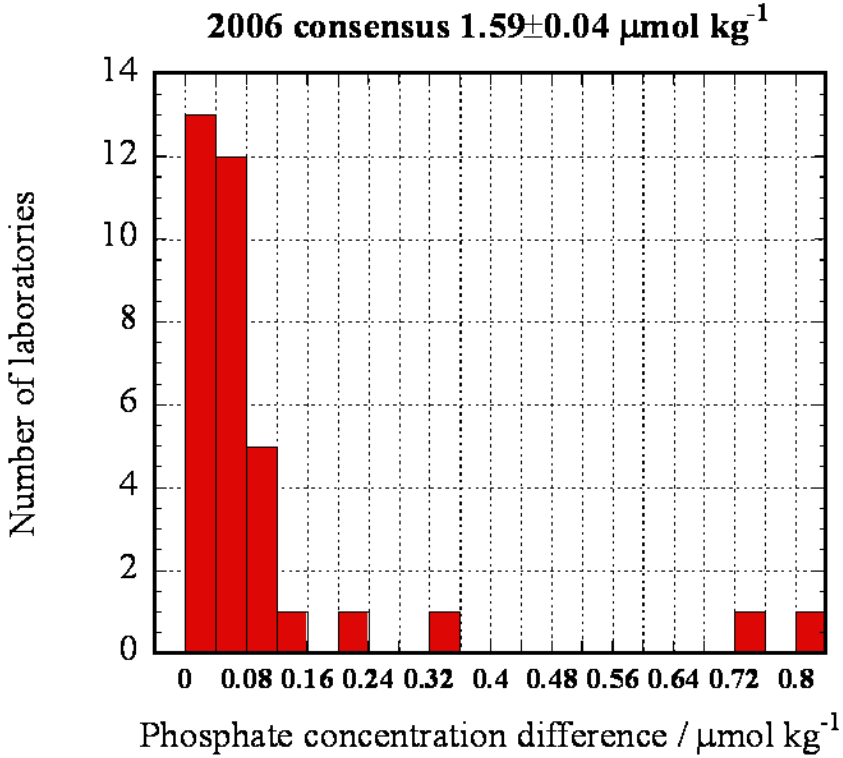


Figure 9. **Comparability** of phosphate concentrations measured at the same laboratory in 2006 and 2008 I/C studies.

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, 134 pp.

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}

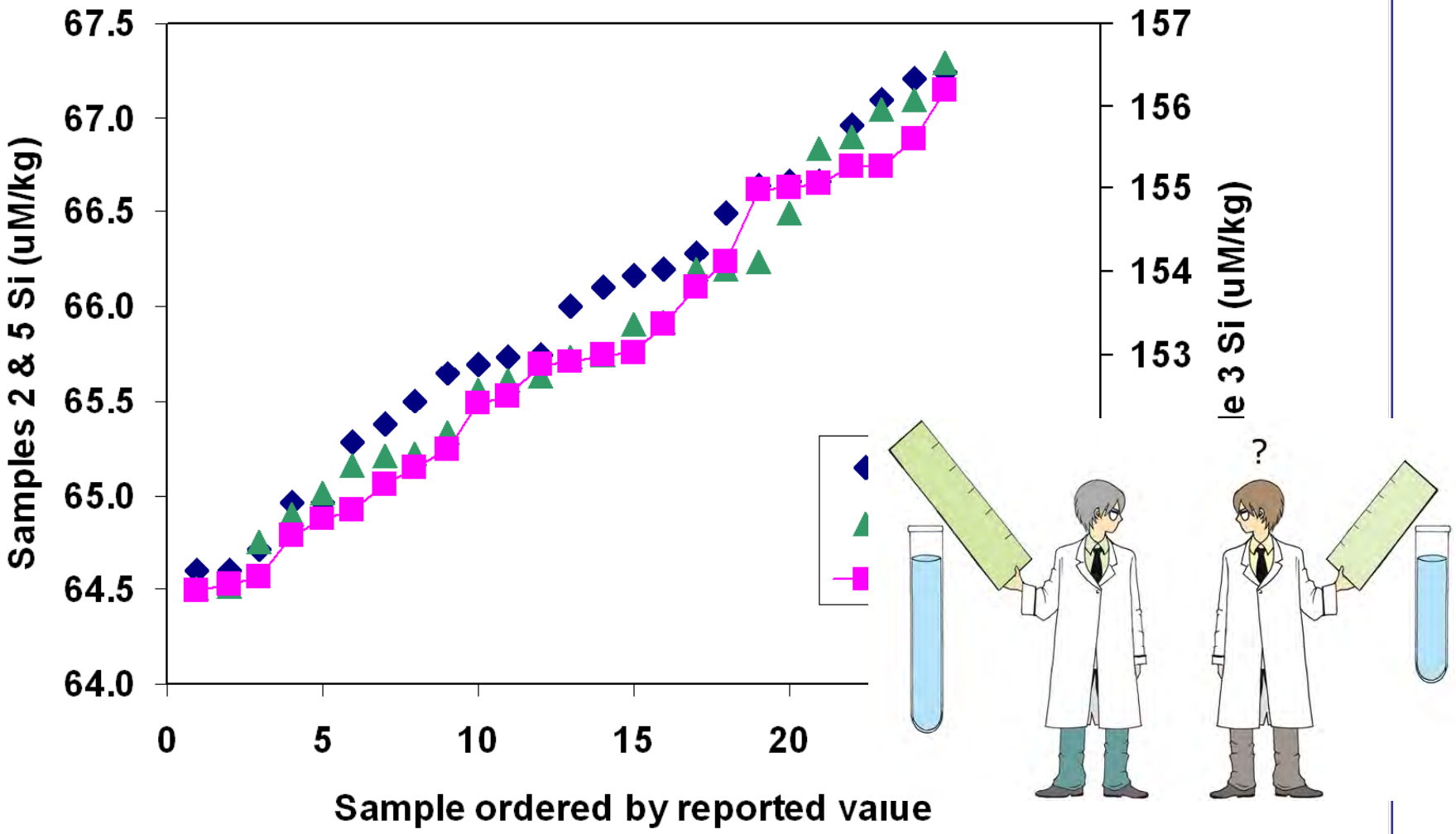
Ammonia: TBD

DOM: TBD

Uncertainties should be stated with each concentrations of nutrients

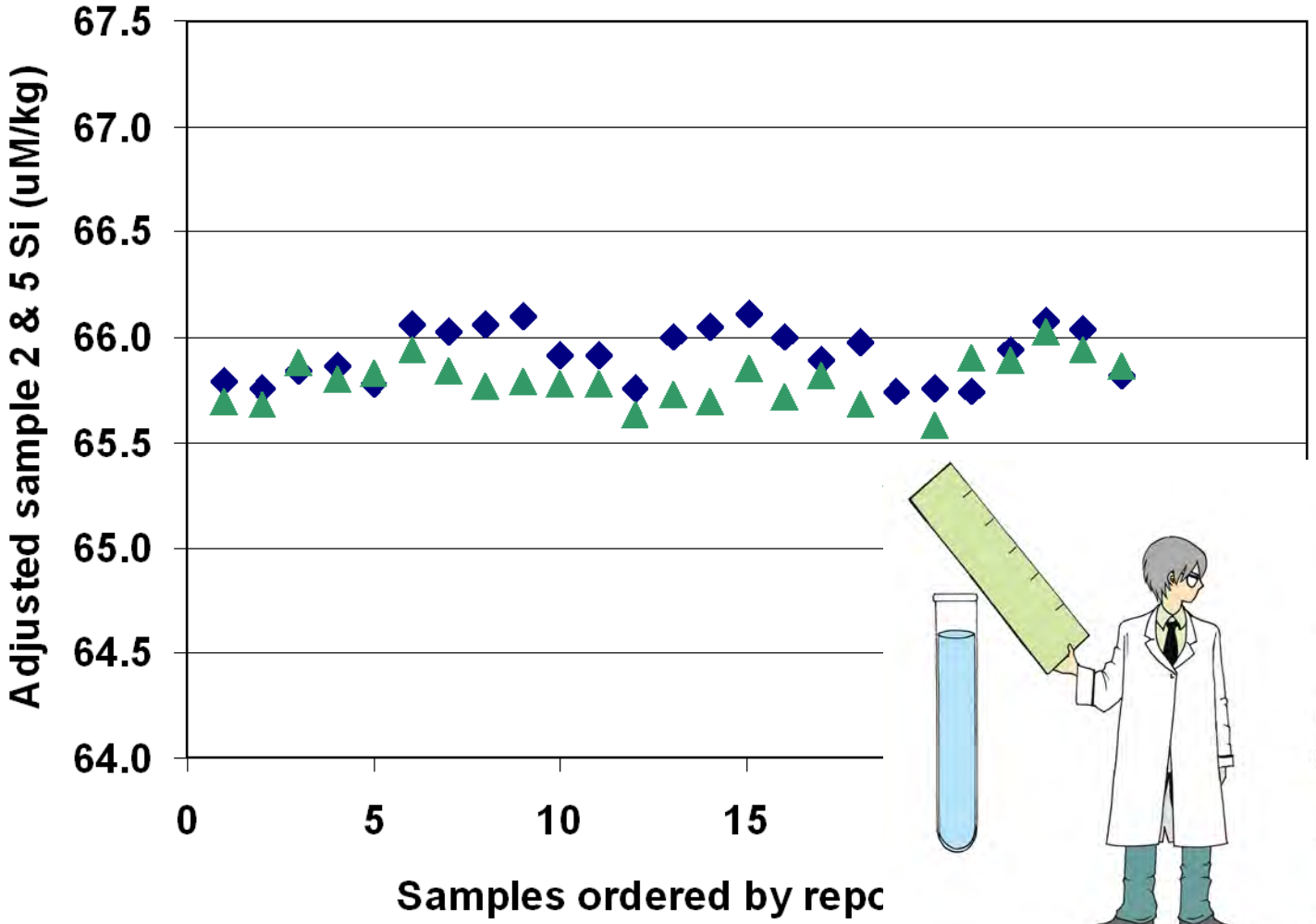
※**DOM**: Dissolved organic matter

Illustrating the effect of an International Nutrients Scale System



Aoyama, M. & Co-Authors (2010). "A Joint ICES-IOC Study Group On Nutrient Standards" in Proceedings of OceanObs'09: Sustained Ocean Observations and Information for Society (Annex), Venice, Italy, 21-25 September 2009, Hall, J., Harrison, D.E. & Stammer, D., Eds., ESA Publication WPP-306.

Illustrating the effect of an International Nutrients Scale System



Aoyama, M. & Co-Authors (2010). "A Joint ICES-IOC Study Group On Nutrient Standards" in Proceedings of OceanObs'09: Sustained Ocean Observations and Information for Society (Annex), Venice, Italy, 21-25 September 2009, Hall, J., Harrison, D.E. & Stammer, D., Eds., ESA Publication WPP-306.

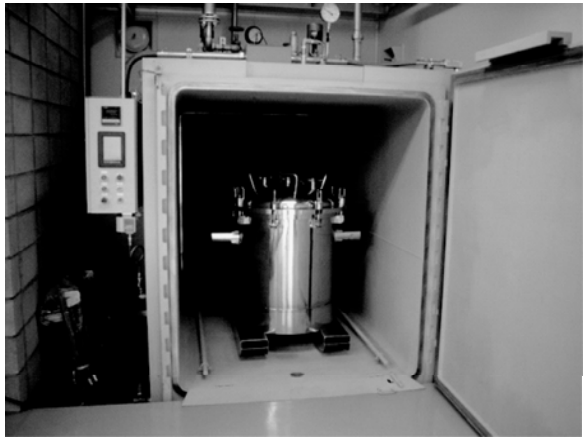
How to obtain the comparability of nutrient measurements by INSS?

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

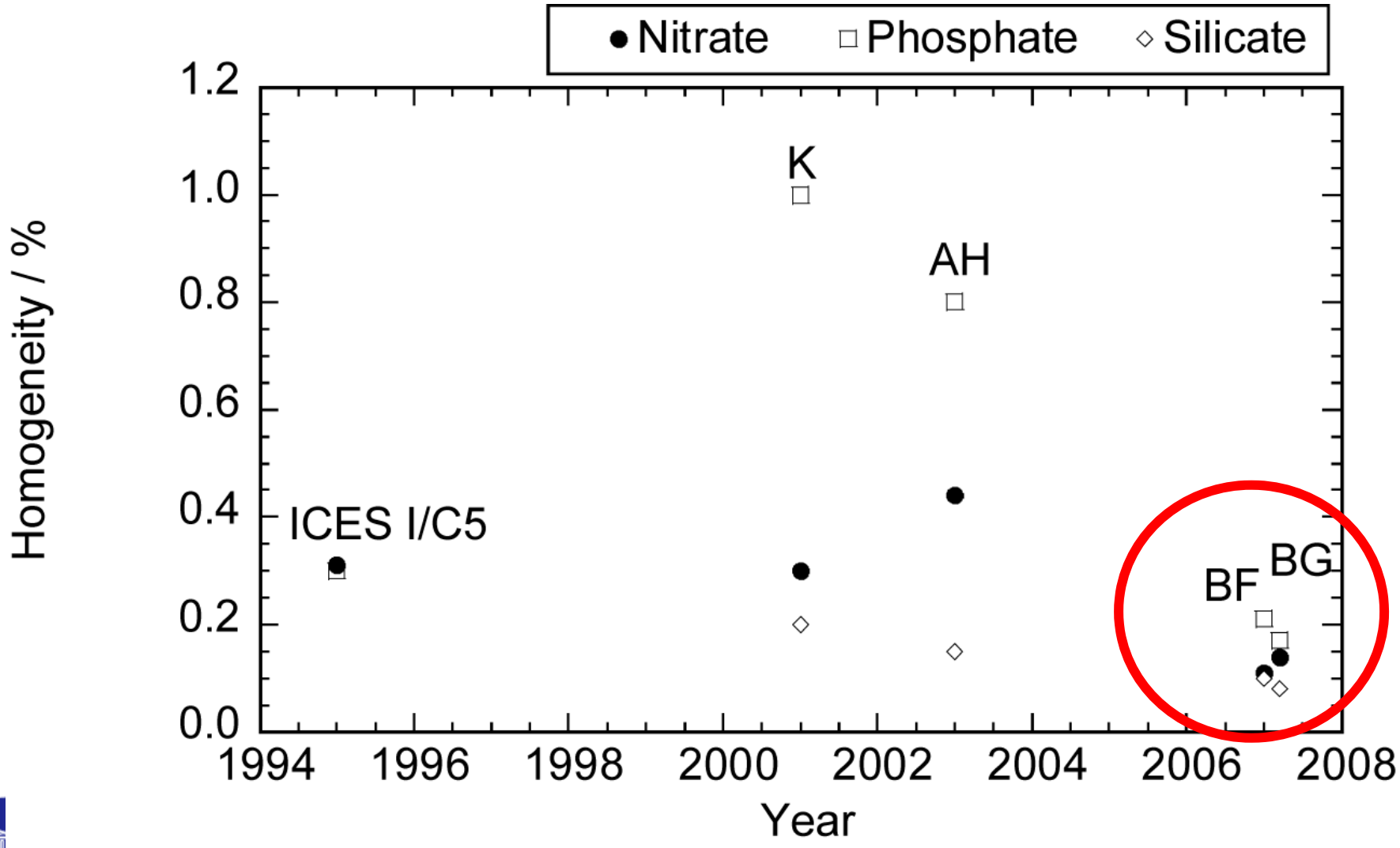


Walk-in autoclave and
230liters tank.
Now 350 liters.
2000 bottles of RMNS per a lot.
3500 bottles soon.

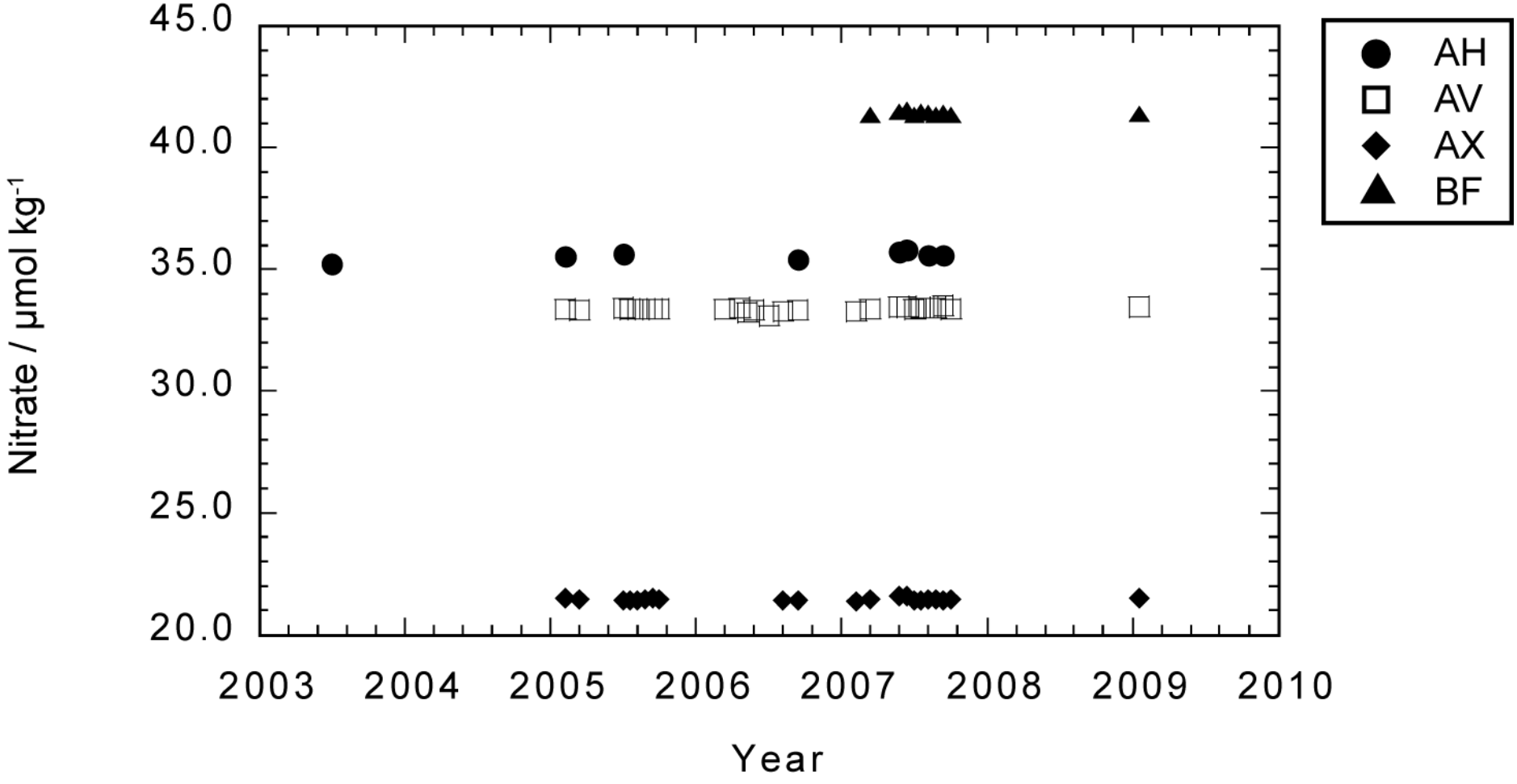
Clean room

RM in alminum bag

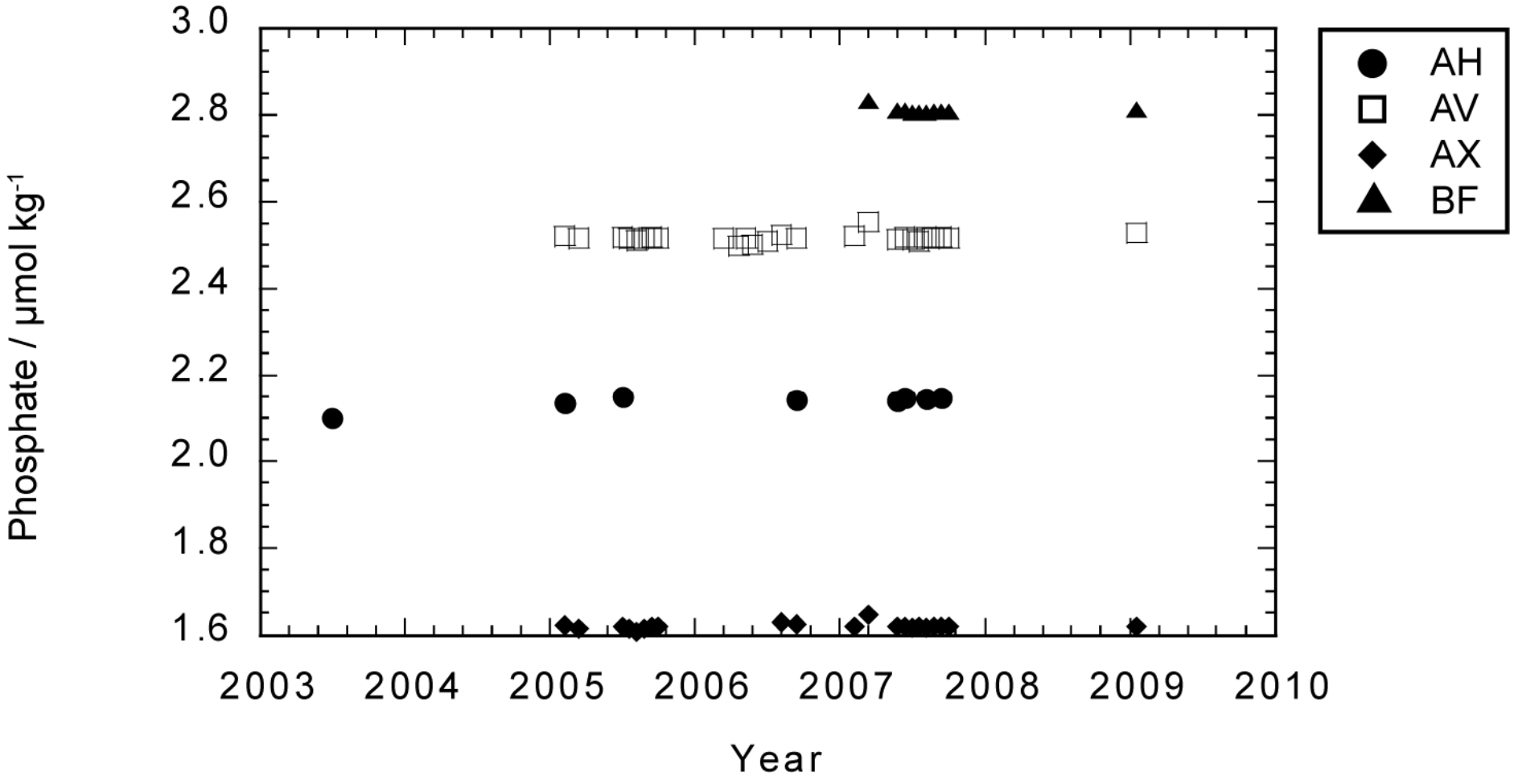
Homogeneity of RMNS



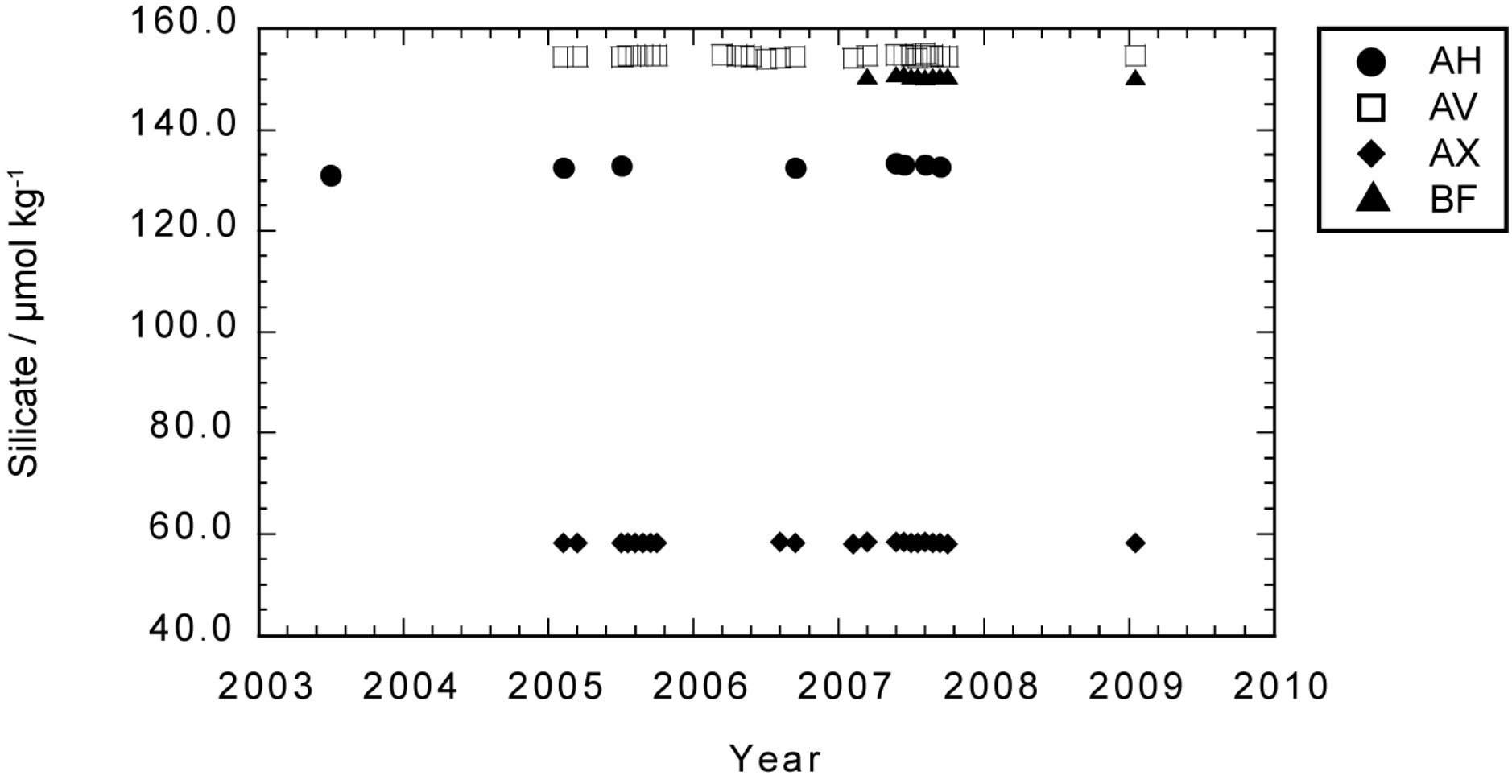
Stability of RMNS: Nitrate



Stability of RMNS: Phosphate



Stability of RMNS: Silicate



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.

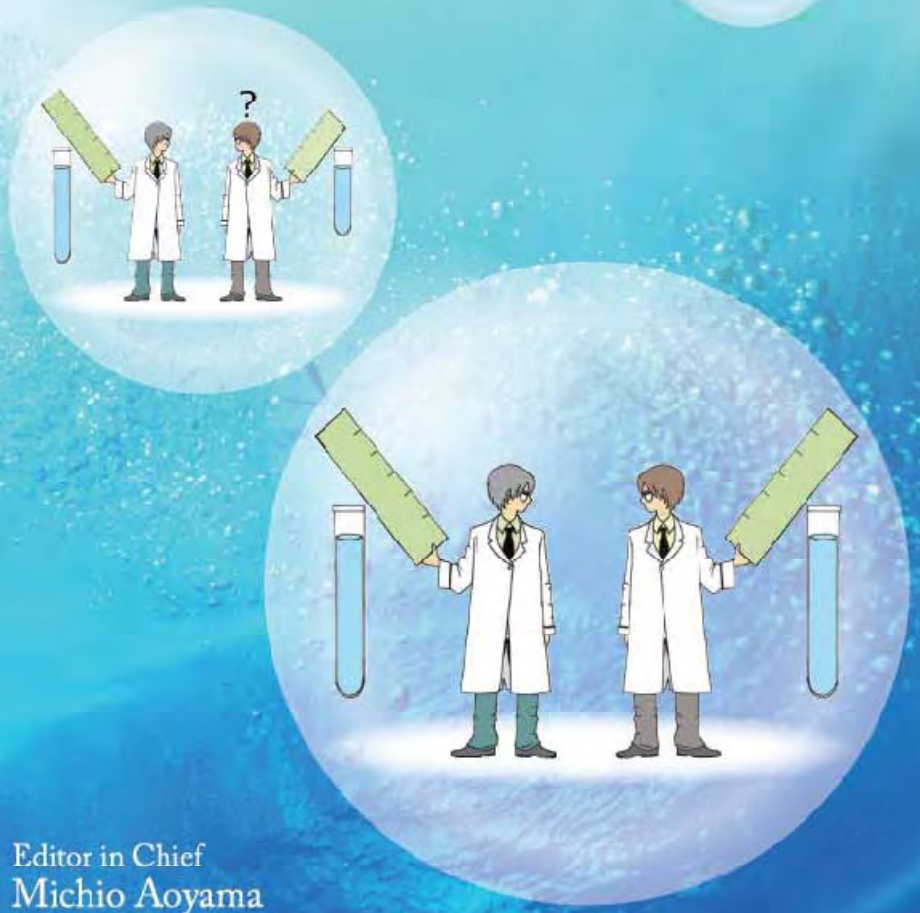
※**RMNS**: Reference Materials for Nutrients in Seawater

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

IOC

Thank you for your attention