Proposal for a SCOR Working Group on an

"International Nutrients Scale System" to improve the global comparability of nutrient data

1 Introduction

Measurements of nitrogen (as NO_3), phosphorus (as PO_4), and silicon (as $Si(OH)_4$) are fundamental for much oceanographic work in hydrography, biogeochemistry and biology. For example, accurate measurements of the nutrients are essential for tracing the uptake of anthropogenic carbon into the ocean. They can also be used for tracing changes in the deep ocean that are crucial to our understanding of global change. However, at the current time the reliabilities of such assessments are uncertain, due to the lack of widely useable reference materials that would allow complete confidence in comparing crucial data sets, from different laboratories worldwide. Large global observing programs (e.g., CLIVAR), and more local projects, require more-comparable information to support assessments of the health and productivity of coastal oceans, changes to the deep oceans, sustainability of marine ecosystems, and predictability of climate change, as well as other processes that affect the Earth's population on many levels. The accuracy of chemical oceanographic measurements depends on calibration against certified reference materials to ensure comparability over time and among laboratories world-wide. In 2002, a U.S. National Research Council (USNCR) report (Dickson et al., 2002) clearly stated that key parameters (including nutrients) lacked reliable and readily available reference materials. Comparability of nutrient and other data over time and among different research groups is urgently needed. The USNRC report identified the most urgently required chemical reference materials based on certain key themes for oceanographic research. At the top of the report's list of the new reference materials needed were standards for the measurement of nutrients. The report stated: "There is an urgent need for a certified reference material for nutrients. Completed global surveys already suffer from the lack of previously available standards, and the success of future surveys as well as the development of instruments capable of remote time-series measurements will rest on the availability and use of good nutrient reference materials." Similarly, the IPCC Report in 2007 highlighted the current problem inherent in comparing existing data sets: "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" (Bindoff et al., 2007).

Marine chemists have, however, been active in the pursuit of establishing reliable comparability of nutrient measurements. The history behind this is described in section 3 below. A consensus has been achieved in realizing (i) the limits imposed on the work by the purity of "off-the-shelf" chemicals, (ii) the form that reference materials should take, (iii) the quantities that they would need to be produced in, and (iv) that use of the reference materials would also need to be accompanied by adherence to "best practice for their use". To guarantee comparability of data from different laboratories and from different research cruises, a single international "scale" for nutrients needs to be developed, and then recommended for use throughout the world-wide marine chemistry community. This has already been achieved by the use of Certified Reference Materials (CRMs) for measurements of the CO_2 system (Dickson, 2003; 2010).

We are now in a position where the tools are available for this goal to be achieved. An equivalent to the carbonate systems CRM has now been developed for nutrients. These are the RMNS (Reference Materials for Nutrients in Seawater) produced by KANSO (General Environmental Technos Co., Ltd.) in Japan. They are being produced on a large enough scale to meet global demand, and are being independently certified by the Metrology Institute of Japan. But, as in the case of CRMs for CO_2 measurements, the adaptation of RMNS will depend on trust being developed in these materials in laboratories around the world and their availability being matched to appropriate best practice in their use.

We see this being taken forward as an "International Nutrients Scale System (INSS)" for seawater analysis, to establish comparability and traceability of nutrient data in the ocean. A major challenge with this work and one which is particularly important for the study of changes in properties of deep water masses is to develop a system by which the data within laboratories and between laboratories is comparable at the 0.1 % level. This should be both within individual cruises and extend to allowing comparison between cruises separated by decades.

The WOCE guidelines published in 1991 (Joyce et al., 1991) suggested that this level of precision (0.1 %) was achievable by the better laboratories individually. However, this level of relative accuracy has not been achieved between laboratories. The aim for INSS is to put into place the tools needed for the improvement of inter-laboratory precision. Key

to achieving the required accuracy is having reliable RMNS which enable the linkage of data between laboratories.

Getting and maintaining accuracy down to the 0.1 % level will be a two-stage process. Firstly the RMNS are being certified by the National Metrology Institute of Japan (NMIJ), but this certification stops at a level of uncertainty (expanded uncertainty of measurement stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approximately 95%.) around 1.0 % for Nitrate and Silicate, but only around 5 % for Phosphate. At the moment the process of testing that the RMNS are stable at the 0.1 % level is underway. (A task of the SCOR working group would be to determine that the producer is achieving this level of stability.) The next stage is to agree a method for assigning values to the RMNS to an accuracy of 0.1 %. This task requires two things (1) consensus between laboratories (who can demonstrate they are producing data which is internally consistent at the 0.1 % level) on the assigned value, and (2) a system for carrying forward in time the assignment of values which will be consistent over decades.

We envisage that a SCOR working group would be the most effective method of developing the INSS concept, with, and for, the global oceanographic community.

2 Terms of Reference

1. **The Working Group will develop and publish on the Internet the algorithm [the set of tools / the RMNS / the laboratory methods and the data reporting chain] needed to implement an international nutrients scale system**. A paper will be submitted to *EOS* or other publication to publicize the algorithm. This will thus begin the process to unify global measurements of nutrients in the marine environment based on the use of reference materials for nutrients in seawater (RMNS).
2. **The Group will submit a session to an AGU meeting (2013) to call for papers on the use of reference materials in the marine environment. This session will also inform the scientific community of the nutrient CRMs available and the developments and results so far for using these standards.**
3. **The Group will consider and report on how effective feedback loops would be established between data generators, database managers, and data users, so that effective alignment of and complete traceability of any future measurements of nitrate, nitrite, phosphate and silicate in seawater would be**

achieved. This will require the development of standardized data-handling procedures, and common data vocabularies and formats across producers and users, and would also include the future linking of national data archives. The group will seek to involve several national and international data center representatives to assist with this task.

4. **The Group will report on a plan for the promotion of the INSS in the global marine observing community.** This will include:- (a) reporting of the results from previous global stability tests [see list at end for countries involved[i] in 2012, and also a world Map]; (b) promote the wider global use of RMNS by arranging training workshops to encourage their use and training in best practice in developing countries; (c) continuing regular global inter-comparison studies, to continue on from the previous exercises in 2003, 2006, 2008 and 2012[ii].
5. **The GO-SHIP nutrients measurement manual (Hydes et al., 2009, see http://go-ship.org/Manual/Hydes_et_al_Nutrients.pdf) will be updated to include detailed protocols for the use of the RMNS solutions and the reporting of the analytical results.**
6. **A plan will be developed and written for transitioning to a self-financing scheme after the end of Japanese Government research funding in 2014**[iii], based on the experiences of other similar programs.
7. **The Group will report a plan for continuing to (i) guide the work of the accredited Japanese company**[iv] **currently producing the RMNS solutions, and (ii) work with the National Metrology Institute of Japan on certification of the accuracy the RMNS solutions.**

3. History of the development of the RMNS:

In the 1990's, a number of studies were organized under the ICES umbrella. These studies were well documented (UNESCO, 1965, 1967; ICES, 1967, 1977; Kirkwood, 1991; Aminot et al., 1995 and Aoyama, 2006). In Europe, this led to the establishment of the Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME: Topping, 1997). QUASIMEME is a useful programme for validating the procedures of individual laboratories for a wide range of determinands. However, this programme is inadequate for supporting the traceability that is required to link day to day measurements in order to improve the overall precision within a laboratory, or to achieve a known level of comparability between different laboratories.

In 2000 and 2002, the National Oceanic and Atmospheric Administration (NOAA), USA and the National Research Council of Canada (NRC) conducted two inter-comparison exercises to certify the MOOS-1 reference material (Willie and Clancy, 2000; Clancy and Willie, 2003). However, despite these individual efforts, adequate comparability and traceability of nutrient data have not yet been achieved. Various other efforts were made to attempt to improve the situation, but these were on too small a scale to meet the needs of the global community in measuring nutrients in seawater.

In 2003, Michio Aoyama of the Meteorological Research Institute (MRI), Japan, organized an inter-laboratory comparison study that included 18 laboratories (Aoyama, 2006, Aoyama et. al, 2007). In 2006 and 2008, Dr Aoyama, working with Hidekazu Ota of the General Environmental Technos Co., Ltd. (KANSO), Japan, organized the second and third inter-comparison studies that included more than 55 laboratories world-wide (Aoyama et al., 2008; 2010). These inter-laboratory comparison studies clearly showed that the global use of reference materials for nutrients in seawater would greatly improve the comparability of nutrients data in the world's oceans.

In early 2007, Michio Aoyama visited the National Oceanography Centre in Southampton, UK, to discuss the results of the 2006 inter-laboratory comparison study with the European participants in the exercise as well as other interested nutrient chemists. As a follow-up to this meeting, an International Workshop on Chemical Reference Materials in Ocean Science was held in Tsukuba, Japan, in late 2007. It focused on the measurement of nutrients and of ocean CO_2 parameters, and the then-current status of available chemical reference materials, particularly for nutrients. The participants agreed to start a collaborative programme, called the International Nutrients Scale System (INSS), with the aim of establishing global comparability and traceability of nutrient data.

In February 2009, that INSS group held a workshop at UNESCO in Paris to advance international collaboration and to discuss future tasks with a wider group (2009 International Nutrients Scale System international workshop, Paris, 10–12 February 2009). An "International Nutrients Scale System (INSS)" in seawater was agreed as the appropriate way to achieve this goal. This led to the setting up of a Study Group on Nutrient Standards (SGONS) supported by IOC and ICES between 2010 and 2012.

This IOC-ICES SGONS group has (i) worked alongside the Japanese Metrology Institute who are certifying the RMNS; (ii) collaborated with KANSO on testing the stability of the

RMNS materials; (iii) Discussed results on work developing associated standards for (a) organic carbon, (b) organic nutrients, (c) dissolved oxygen, (d) mercury-free standards for the carbonate system; (iv) Organised an expanded (in terms of global coverage) inter-comparison exercise including 69 labs in 2012; (v) Initiated plans and applications for an at-sea inter-comparison study to take place in 2014, and (vi) Considered the steps necessary to encourage the global uptake of RMNS to the level that has been achieved by the IAPSO Standard-Seawater for the measurement of salinity, and measurements of total dissolved inorganic carbon and alkalinity.

The next phase in the progression to the global acceptance and use of these nutrient CRM's, would be by the establishing of a SCOR Working Group.

4. Membership of Working Group:

Full Members

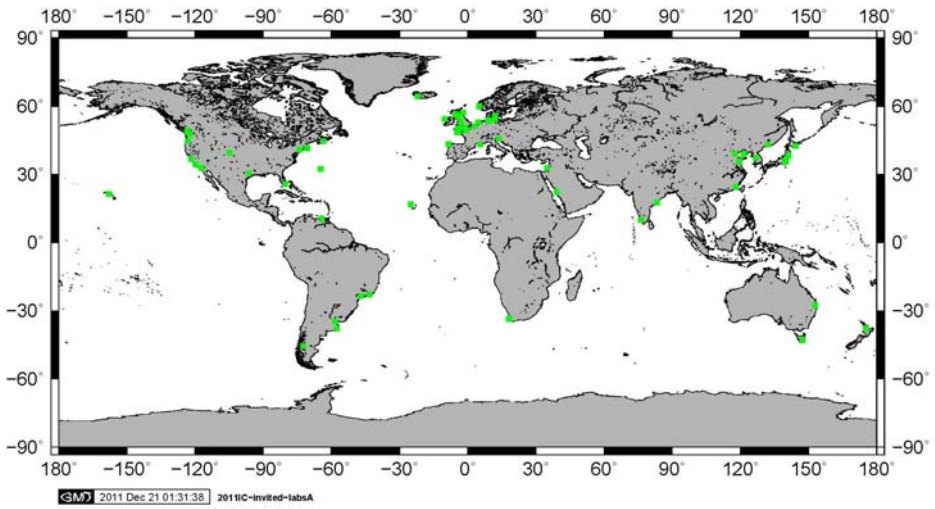
1	Michio Aoyama	Japan	Chairman
2	David Hydes	UK	Co-Chairman
3	Jan van Ooijen	Netherlands	Measurement methods
4	Toste Tanhua	Germany	Comparability of deep sea data
5	Steve Diggs	USA	Standard data reporting, data vocabularies
6	Malcolm Woodward	UK	Low level measurements
7	Andrew Dickson	USA	CRM experience
8	Akiharu Hioki	Japan	Metrology & Certification
9	Minhan Dai	China	Large global (LOICZ and Chinese) programs
10	Susan Becker	USA	CLIVAR/GO-SHIP hydrography

Associate Members:

Additional input to the group will be invited from a range of experts. Where necessary financial support for attending meetings with the core SCOR group will be supported through MRI Japan (Grant number "Kiban-S 23221003" of Grants-in-Aid for Scientific Research of Japan Society for the Promotion of Science (JSPS), made to Michio Aoyama). People involved would include: Masanobu Katagiri, KANSO Japan, on RMNS

production; Alex Kozyr, USA, on experience of multiple user database access (e.g., SOCAT); Karel Bakker, Netherlands, and Anne Daniel, France, on analytical methodologies; Jim Swift, USA and Bernadette Sloyan, Australia, Clivar-GO-SHIP; Mario Hoppema, Germany and Bob Key, USA, comparability of deep sea data; Takeshi Yoshimura, Japan, on organic nutrients; and Akihiko Murata, Japan, on related materials for carbonate work.

The group will be linked to the development of the FOO (Framework of Ocean Observations) effort by the input from Toste Tanhua (currently Chairman of the International Ocean Carbon Coordination Project: IOCCP). At a more local level, the group will also promote the activity with, for example, ICES and PICES (e.g., David Hydes' work as part of the ICES Marine Chemistry Working Group.)



Map showing the locations the laboratories taking part in the 2012 INSS inter-comparison exercise.

5 References

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Endnotes

[i] Argentina, Australia, Belgium, Bermuda, Brazil, Canada, Cape Verde, Chile, China, Denmark, France, Germany, Iceland, India, Israel, Italy, Japan, Netherlands, New Zealand, Norway, Russia, Saudi Arabia, South Africa, South Korea, Spain, UK, USA, Venezuela.

[ii] The frequency of the international collaborative inter-comparison exercises would be every five years.

[iii] Michio Aoyama funded by grant in aid for scientific research of Japanese Government Grant number “Kiban-S 23221003“ of Japan Society for the Promotion of Science (JSPS) entitled “A study of the inventory and distribution of seawater nutrients together with higher comparability” (April 2011 to March 2014)

[iv] KANSO-TECHNOS Japan. KANSO achieved an accreditation as “Reference Material Producers” on 27 April 2011. The accreditation criteria are according to ISO Guide 34 + ISO/IEC 17025.