Proposal for a SCOR Working Group:
Towards harmonization of global oceanic nutrient data

Rationale

One of the major challenges for the future of planet Earth will be the accurate observation of changes to both the upper water column and also to deep oceanic waters, in particular with respect to carbon and dissolved nutrients, with the important requirement to be able to detect global changes in geochemical cycles. We therefore need to be able to reliably compare results for oceanic waters from different sources, with total confidence However, there are currently no mechanisms for global consensus to obtain consistently accurate nutrient data. We believe that there is a requirement for laboratories around the globe involved in these studies to harmonize their analytical outputs of global oceanic nutrients in order to achieve this aim of accurate comparisons. We also recognize the importance of quality and harmonization in coastal and shelf water nutrient analysis, but here we focus only on the important scientific question of any climate-induced changes to the upper and deep oceanic nutrient regimes. The significance of harmonization of a number of other important ocean processes such as, temperature measurements (ITS90, traceable to SI using Standard Platinum Resistance Thermometer, SPRT), salinity measurements (comparability ensured using IAPSO salinity standard seawater provided by OSI, UK) and carbonate system parameter measurements (comparability and traceability ensured using CRMs provided by Dickson's laboratory, SIO, USA, Dickson, 2003; 2010), have already all been established.

Since 1965 there have been a number of inter-laboratory comparison studies, of various magnitudes, that have been conducted to investigate the comparability of nutrient analyses between laboratories. These were led by UNESCO, ICES, NOAA/NRC, QUASIMEME and MRI (UNESCO, 1965, 1967; ICES 1967, 1977; Kirkwood, 1991, Aminot and Kirkwood., 1995; Topping, 1997; Willie and Clancy, 2000; Clancy and Willie, 2003; Aoyama et al., 2006, 2008, 2010, 2013), and recently the updated nutrient analytical manual based on best practices (GO-SHIP manual by IOC-ICES Study Group on Nutrient Standards (SGONS), Hydes et al 2010) has been published. These initiatives have all aimed at contributing to improving nutrient analysis and comparability during these several decades. However, there has never yet been a properly coordinated effort to harmonize these studies and allow us to combine results from different laboratories with confidence. This will be the first step in allowing us to be able to detect any changes to oceanic nutrients over time, and open the opportunity of determining how these changes are affecting global geochemical cycles.

The IPCC Report in 2007 highlighted the current problem inherent in comparing existing data sets stating that: "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). Actually, results of global crossover station analysis showed discrepancies of up to 10 % for deep nutrient data during the last three decades (Aoyama et al., 2013), and the results

of inter-laboratory comparison studies since 2003 showed a similar magnitude of discrepancy among some of the participant laboratories (Aoyama et al., 2007; 2008; 2010). This also indicates that analytical problems may cause larger discrepancies for deep water nutrients. Although this situation has been improved somewhat, it is still difficult to ascertain with any certainty temporal changes in ocean nutrients. We can however now detect changes in deep ocean temperature (and hence heat content) (Levitus et al., 2009; 2012; Kouketsu et al. 2009) from observations due to their relatively larger changes compared with those in nutrients, and comparability of temperature measurements are possible in the order of mK. Changes to the carbonate system parameters in the deep ocean are also reported with comparability being ensured by the use of CRMs (e.g. Wanninkhof et al., 2010, Ríos et al., 2012, Khatiwala et al., 2012). Similarly, changes to the oceanic oxygen can now be accurately observed (Stendardo and Gruber, 2012).

If we can establish mechanisms to harmonize the quality of oceanic nutrient data, we will be able to detect changes in nutrient levels due to human impact and shifting physical processes, which might alter the supply of nutrients to the upper ocean and/or due to changes of ocean circulation which might be the cause of changes to nutrients in deep waters. Improved comparability of nutrient concentrations in the water column will also help us to improve estimation of the anthropogenic portion of the observed increase of total carbon in the water column.

Marine chemists have previously been active in the pursuit of establishing reliable comparability of nutrient measurements. A consensus was achieved through the former IOC-ICES Study Group (SGONS – Study Group on Nutrient Standards, 2009-2012) activity 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 would need to be produced for global use, and (iv) that use of the reference materials would also need to be accompanied by adherence to “best practice for their use”.

To properly guarantee comparability of data from different laboratories and from different research cruises, the precise mechanisms for a global consensus for nutrient levels need to be developed. This will foster a move towards the harmonization of nutrient data using globally accepted RMs/CRMs, followed by the recommendation of protocols for their use throughout the world-wide marine chemistry community. This has already been achieved both by the use of CRMs for measurements of the CO_2 system, and the use of the IAPSO standard seawater for salinity measurements.

The situation now calls for further international collaboration through SCOR, and a Working Group to establish the mechanisms required to harmonize the quality of oceanic nutrient data, using globally accepted RMs/CRMs. A major challenge with this SCOR WG 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 comparability of data within and between laboratories is better than 0.2 % at full scale of nitrate, phosphate and silicate concentration. This level of comparability has already been achieved for the measurement of total carbon.

This objective should be the goal for data generated during individual research cruises and extended to allowing comparisons between cruises separated by decades. The experiences of this SCOR WG will also give positive feed-back to the scientific communities of coastal ocean observatories, and for researchers developing nutrient sensors for buoys and floats, by providing and recommending globally accepted RMs/CRMs for the calibration of instruments and sensors, and providing globally accepted analytical methods based on best practices. Such feedbacks will move towards the goal of achieving comparability of nutrient data throughout the oceans, which will have been obtained by different methods, instruments, and technologies.

A recent Framework of Ocean Observing (FOO) statement introduced the concept of Essential Ocean Variables (EOVs), and the assessment and development of readiness for sustained observations, with the aim of promoting collaboration in developing requirements, observing networks, and data and information streams. Nutrients are identified as one of these EOVs (Fischer & Grimes, 2013).

We propose that a SCOR working group would be the most effective and timely way to now develop the mechanisms to harmonize nutrient data using globally accepted RMs/CRMs with, and for, the global oceanographic community, and for it to become involved through SCOR and promote the global use of CRMs for oceanic nutrient analysis. This initiative will be based on previously developed collaboration with the IOC-ICES SGONS which ended in 2012. For future generations it is unacceptable to produce historical data sets without having an acceptable reference scale for multi-year comparisons.

Scientific and Technological Background

Measurements of nitrogen (as NO_3), phosphorus (as PO_4), and silicon (as $Si(OH)_4$) are fundamental requirements for oceanographic studies of hydrography, biogeochemistry and biology.

For example, accurate measurement of nutrients is essential for tracing the uptake of anthropogenic carbon into the ocean and is also essential for observing changes in deep ocean dissolved nutrients, all as a part of the global changes to geochemical cycles. However, at the current time, the reliability of such assessments are uncertain, due mainly to the lack of widely useable reference materials that would allow for more confidence when comparing crucial data sets, taken from different laboratories worldwide.

Large global observing programs 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 global comparability over time.

In 2002, a U.S. National Research Council (USNRC) report (Dickson et al., 2002) clearly stated that key parameters (including nutrients) lacked reliable and readily available reference materials. 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". Since that time there have been developed a number of reference materials for oceanographic use have been developed i.e., a Danish RM, NRC-Canada RM, and one developed by KANSO-Japan. The responsibility for resource seawater sampling, onboard pasteurization and the distribution of this RM will be taken on by JAMSTEC (Japan Agency for Marine-Earth Science and Technology), which will distribute the RM globally, in the same manner as the carbonate system CRMs from Dickson's laboratory (SIO, Scripps).

The WOCE guidelines published in 1991 (Joyce et al., 1991) suggested that levels of precision (0.2% of full scale for nitrate and silicate concentrations, with 0.4 % for phosphate concentrations) were achievable by the better performing laboratories individually, without RMs/CRMs. However, this level of relative precision has not actually been achieved between laboratories. We need to put into place the tools needed for the improvement of inter-laboratory precision. Key to achieving the required accuracy is having reliable RM's which enables the linkage of data between laboratories.

In-situ nutrient sensors are a future nutrient analytical technology that needs addressing and hence the need for their use of CRM's to be able to give confidence to the output data quality. Currently there is the Alliance of Coastal Technologies (ACT) group which has had 2 previous workshops devoted to nutrient measurements by sensors (ACT 2003; 2006), and we would look to include representatives from this sensor group in the future international inter-calibration exercise.

Terms of Reference and products

ToRs:

1. The Working Group will assess the homogeneity and stability of currently available RMs/CRMs. It will also determine if the currently available producers are achieving a level of precision within and between laboratories which is comparable to or better than 0.2 %. This task requires two things;- consensus on the assigned value between laboratories (which can demonstrate they are producing data which is internally consistent at the 0.2 % level) , and a system for carrying forward in time, the assignment of values which will be consistent over decades.
2. The Working Group will consider and report on how effective feedback loops could 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, with common data vocabularies and formats across producers and users, and would also include the future linking of national and international data archives. The group will seek to involve international data center representatives to contribute to and lead this task.

3. The Group will report on a plan for the promotion of the use of RM in the global marine observing community. This will include:- (i) reporting of the results from previous global stability tests [see list at end for countries involved in the 2012 exercise]; (ii) promoting the wider global use of RM's by arranging workshops to actively encourage their use and to provide training in best practice particularly in developing countries, and (iii) continuing regular global inter-comparison studies, following on from the previous exercises in 2003, 2006, 2008 and 2012, with collaboration with funding by the IOCCP-SSG in 2014/2015.
4. The GO-SHIP nutrients measurement manual which was a product of the IOC-ICES SGONS (Hydes et al., 2009, see http://go-ship.org/Manual/Hydes_et_al_Nutrients.pdf) will be updated as part of this SCOR WG to include detailed protocols for the use of the RM solutions and the reporting of the analytical results based on a NIOZ/PML analytical workshop held in late 2012.

Products:

The WG will write an article for publication in EOS after its first meeting in early 2014 to inform the international community about the objectives and future plans of the SCOR WG. Talks and posters will be presented at the first Workshop proposed to be held at Ocean Sciences 2014 as to the current situation with regard to the issues of RM's, intercalibration exercises and issues related to the quality analysis of nutrients.
Also, a written document will be produced from each WG meeting.
As a final product there will be produced a "best practices" manual which will provide the community with a recommended consistent approach to the sampling, analysis, use of RM's, quality control of nutrients, and the subsequent data handling

Meetings

Kick-off Meeting: Upon funding, the WG will have a kick-off meeting in early to mid 2014. In order to provide good international visibility, the most suitable international platform would be the OSM 2014 (February 23-28 2014, Hawaii, USA), where a workshop on changes of nutrients in the world's oceans and use of RMs/CRMs will be held, or alternatively this will be proposed at the 2014 EGU General Assembly (April 27 – 2 May 2014, Vienna, Austria).

Main Meetings: Two main WG meetings will be held – one about half-way through and the other one towards the end of the WG lifetime in 2017. Potential venues for the half-way meeting are the AGU fall meeting in 2015 or the 2016 Ocean Sciences Meeting. Candidates for the final meeting could be the 2017 AGU fall meeting or 2017 EGU General Assembly.

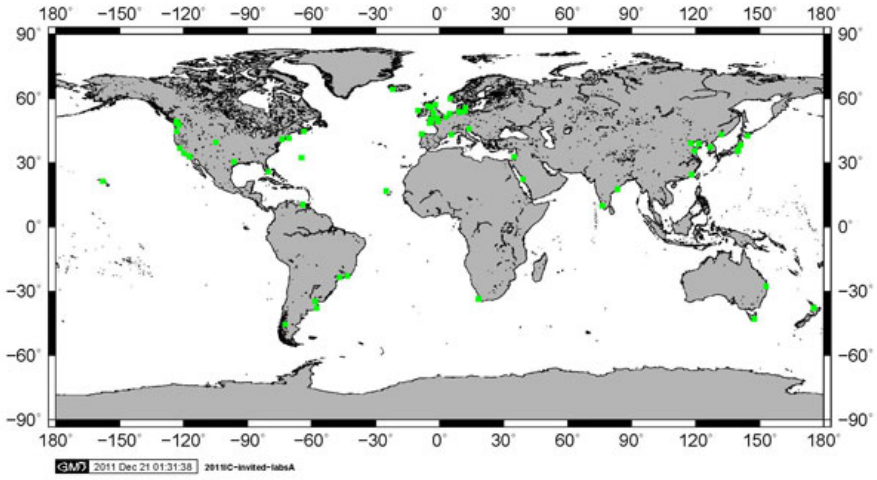
Capacity building

This important aspect is reflected in two ways. The first is to promote participation of developing countries in inter-laboratory comparison studies of RM's through the POGO involvement. Secondly, is to invite participating laboratories to a 3-day workshop in 2015 planned to be held at the Scripps Institution (SIO), USA (depending on additional funding) to discuss results of inter-laboratory comparison studies of RM's.

Building capacities in developing countries can be accelerated by providing a good simple manual based on "best practices" and we will encourage greater participation in the future inter-laboratory comparison study of RM's proposed for 2015. The aspect of capacity building could be further augmented by hosting a session (in conjunction with a WG meeting/AGU meeting/OSM meeting), at approximately mid-term, to discuss the needs and capabilities of developing countries with respect to using other suitable programs. We will initially instigate a targeted questionnaire to laboratories in developing countries to highlight their most important analytical needs, this all be accomplished with the help and advice of POGO.

There is also agreement for sea-time to hold a nutrient inter calibration research cruise in late 2014 on the new Australian research ship the RV Investigator. Should the WG be funded then the intention would be to go ahead with this research voyage (potential funding is in discussion) with 6 or 7 global laboratories being represented to make comparative measurements at sea, and to test the use of suitable RM's in the working environment. The WG will also seek funding to host a POGO fellowship to take a scientist from a developing country on this voyage to work alongside experienced nutrient chemists, thus offering a unique training opportunity. This fellowship would also involve pre and post study time at the host laboratory in preparation for the voyage.

The laboratories that took part in the 2012 inter-comparison exercise of nutrients in seawater are shown below. The IOCCP-SSG will fund the next inter-comparison exercise of nutrient reference materials in seawater in 2015, collaborating with this proposed SCOR WG to expand global participation from the 2012 representatives from the following countries: 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. The 2015 inter-calibration exercise will expand this global group with more partners from developing countries.



The WG has been in contact with the Partnership for Observation of the Global Oceans, POGO, to also investigate hosting a nutrient training workshop in 2016 as part of POGO's portfolio of training and education activities.

Membership of Working Group

Full Members:

1. Michio Aoyama, MRI, Japan, Co-Chair, geochemistry (M)
2. Malcolm Woodward, PML, UK, Co-Chair, Low level precision measurements (M)
3. Toste Tanhua, GEOMAR, Germany, Chairman of the International Ocean Carbon Coordination Project: IOCCP (M)
4. Andrew Dickson, SIO, USA, CRM experience (M)
5. Bernadette Sloyan, CSIRO, Australia, CLIVAR/GO-SHIP (F)
6. Anne Daniel, IFREMER, France, analytical methodologies (F)
7. Susan Becker, SIO, USA CLIVAR/GO-SHIP hydrography (F)
8. Minhan Dai, Xiamen University, China, Large global (LOICZ and Chinese programs (M)
9. Akihiko Murata, JAMSTEC, Japan, Chemical oceanography, Global carbon/nutrient stoichiometry (M)
10. Howard Waldron, Department of Oceanography, University of CapeTown, South Africa (M)

Associate Members:

Trevor Platt, Executive Director, POGO
Alex Kozyr, USA, experience with multiple user database access (SOCAT):
Karel Bakker, NIOZ, The Netherlands sea-going analytical facility:
David Hydes, NOC, UK, ICES Marine Chemistry working group, (ICES/PICES):
Takeshi Yoshimura, CRIEPI, Organic Nutrients
Jonathan Sharp, University of Delaware, USA, DOC RM experience
Akiharu Hioki, NMIJ, Japan, certification of RM
Ralph Sturgeon, NRC, Canada, CRM producer.

FOO project: The group will be linked to the development of the FOO (Framework of Ocean Observations) effort by input from Toste Tanhua (currently Chairman of the International Ocean Carbon Coordination Project: IOCCP).

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Acronyms:

CLIVAR	Climate Variability and Predictability
CRIEPI	Central Research Institute of Electric Power Industry
CRMs	Certified Reference Materials
CSIRO	The Commonwealth Scientific and Industrial Research Organisation
DIC	Dissolved Inorganic Carbon
DOC	Dissolved organic carbon
EOVs	Essential Ocean Variables
EOS	Eos, Transactions American Geophysical Union
FOO	Framework of Ocean Observations
GO_SHIP	Global Ocean ship-based hydrographic investigations program
ICES	International Council for the Exploration of the Sea
IFM-GEOMAR	Leibniz Institute of Marine Sciences - Marine Biogeochemistry
IFREMER	French Research Institute for Exploitation of the Sea
IOC	Intergovernmental Oceanographic Commission
IOCCP	International Ocean Carbon Coordination Project
IPCC AR4	IPCC Fourth Assessment Report
ITS90	The International Temperature Scale of 1990
JAMSTEC	Japan Agency for Marine-Earth Science and Technology
LOICZ	Land-Ocean Interactions in the Coastal Zone
NIOZ	Royal Netherlands Institute for Sea Research
NMIJ	National Metrology Institute of Japan
NRC	National Research Council Canada
PICES	The North Pacific Marine Science Organization
PML	Plymouth Marine Laboratory
POGO	Partnership for Observation of the Global Ocean
RM	Reference Material
RMNS	Reference Materials for Nutrients in Seawater
SCOR	Scientific Committee on Oceanic Research
SGONS	The Joint ICES-IOC Study Group on Nutrients Standards
SIO	Scripps Institution of Oceanography
SPRT	Standard Platinum Resistance Thermometer
SOCAT	Surface Ocean CO2 Atlas
SSG	Science Steering Group
ToR	Terms of Reference

UNESCO	United Nations Educational Science and Culture Organization
USNRC	United States National Research Council
WG	working group
WOCE	World Ocean Circulation Experiment