

SCOR Working Group Proposal

Title: Towards comparability of global oceanic nutrient data

Acronym: COMPONUT

Summary/Abstract (max. 250 words/246)

To better manage the global impacts of human activities on the world's oceans, it is necessary to have accurate observations of changes in carbon and dissolved nutrients in both upper and deep ocean waters. By establishing mechanisms for comparability of nutrient analyses, we will be able to detect changes in nutrient levels due to human impact and shifting physical processes. Such changes could, either alter the supply of nutrients to the upper ocean directly or be from changes to ocean circulation. A recent Framework of Ocean Observing 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 information streams. Nutrients are identified as one of these EOVs. In 2014, two certified reference materials (CRMs) will become available for measurements of nutrients in seawater; a CRM provided by the National Metrology Institute, Japan, and MOOS-3, provided by National Research Council, Canada. The whole situation now calls for further international collaboration through SCOR, with a Working Group to establish the mechanisms for comparable oceanic nutrient data, using globally accepted CRMs. The primary goal is that for nutrient data collected anywhere by one individual laboratory, and data collected over long time periods by one or more laboratories, will be consistent and traceable with certified comparability. For future generations it is unacceptable to produce historical data sets without the absolute consistency necessary to assess spatial and temporal trends.

Scientific Background and Rationale (max 1250 words/1248)

Changes are occurring on a global scale in ocean biogeochemical cycles and much of the cause of these changes, directly or indirectly, is from human activities. Therefore, it is necessary to have accurate observations of trends in carbon and dissolved nutrients in both upper and deep ocean waters. For these observations, it is critical that we can reliably compare results from different laboratories, for geographically similar ocean waters with total confidence. To get a global consensus for nutrient data, it is necessary to both have accepted certified reference materials (CRMs) and to have the requirement to use the CRMs, and these can be established by the authority of a SCOR Working Group. The focus for this proposed Working Group is for oceanic waters, but because the ranges of nutrients expected are similar, the effort can be extended, at least partially, to coastal and estuarine waters. There are currently established certified standardizations for only a few marine parameters; 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 the carbonate system parameter measurements (comparability and traceability ensured using CRMs provided by Dickson's laboratory, SIO, USA, Dickson, 2003; 2010).

The 2007 IPCC Report highlighted the problem inherent in comparing 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). Results of nutrient concentrations from global crossover station analysis have shown 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 participant laboratories (Aoyama et al., 2007; 2008; 2010). This indicates that analytical problems may cause larger discrepancies for deep water nutrients, and these reported comparisons were from a small number of specific studies, whereas there are many oceanic nutrient data sets reported, published, and stored on international databases, with no references to CRMs at all. Although this situation has been improved somewhat, it is still difficult to ascertain with any certainty temporal changes in ocean nutrients. We can now detect changes in deep ocean temperature (and hence heat content) (Levitus et al., 2009; 2012; Kouketsu et al. 2009; Rhein et al., 2013) from observations due to comparability of temperature measurements, on 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 oceanic oxygen can now also be accurately observed (Stendardo and Gruber, 2012).

It is important to now establish mechanisms for improving the quality of reported oceanic nutrient data, which will then allow us to be able to more accurately detect changes in nutrient levels due to human impact and shifting physical processes, which might alter the supply of nutrients to the upper ocean in the future. Improved comparability of reported nutrient concentrations in the water column will also help us to improve estimates of the anthropogenic portion of the observed increase of total carbon in the water column.

To properly guarantee comparability of data from different laboratories, the precise mechanisms of a global consensus for reporting nutrient levels needs to be established. This will foster a move toward the comparability 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 by the use of CRMs for measurements of the CO₂ system, and the use of the IAPSO standard seawater for salinity measurements. A potential problem with using nutrient CRMs is similar to that with the use of references for dissolved organic carbon (DOC); that is, some form of enforcement for their use should be established. There was significant improvement in community DOC measurement during the international JGOFS program due to encouragement by the US National Science Foundation and NOAA to participate in DOC comparability exercises (Sharp et al, 2002). A nutrient CRM SCOR working group should be able to provide the authority for not only certification of nutrient CRMs, but also for their use.

Historically, a U.S. National Research Council report (Dickson et al., 2002) clearly stated that

certain key oceanic parameters lacked reliable and readily available reference materials. That report identified the most urgently required chemical reference materials based on certain key themes for oceanographic research. At the top of the list of the new reference materials needed were standards for the measurement of nutrients, with the statement: “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, RMs/CRMs for oceanographic use have been developed. These include a Danish RM, NRC-Canada CRM (MOOS-3), and one developed by KANSO-Japan. In 2014 NMIJ will start to provide CRMs (NMIJ CRM 7601-a, NMIJ CRM 7602-a, and NMIJ CRM 7603-a) with nutrient concentrations appropriate for the nutrient concentration ranges of Nitrate, Nitrite, Silicate and Phosphate found in the Pacific and Atlantic Oceans. MOOS-3 covers nutrient concentrations specifically for the Atlantic Ocean. Therefore, we now have the opportunity for traceability and comparability of nutrient concentrations throughout the globe, and a mechanism to provide RMs which is traceable to SI through CRMs. Global availability of the RM to traceable to NMIJ CRM will be made through JAMSTEC (Japan Agency for Marine-Earth Science and Technology), in a similar manner to the carbonate system CRMs from Dickson’s laboratory (SIO, Scripps).

A nutrient CRM calls for further international collaboration through SCOR, and a Working Group to establish the mechanisms required to provide comparability of oceanic nutrient data, using globally accepted RMs/CRMs. A major challenge with this SCOR WG is to develop a system by which the comparability of data within and between laboratories is better than 1% at full scale of nitrate, phosphate and silicate concentrations. The levels of comparability achieved for the measurement of oceanic salinity and total inorganic carbon are considerably better than 1%. However, both of those parameters are comparatively simple, chemically, and exist in the open ocean in much narrower concentration ranges than do the inorganic nutrients.

The primary goal for the SCOR Working Group is for nutrient data collected at any one place by an individual laboratory and data collected over long time periods by one or more laboratories to be consistent with certified comparability. The experience of this SCOR WG will also give positive feed-back to the scientific community 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. Such feedback will move toward the goal of achieving comparability of nutrient data throughout the oceans, which will have been obtained by different methods, instruments, and technologies. This initiative will be based on previously developed collaboration with the IOC-ICES SGONS that ended in 2012. For future generations it is unacceptable to produce historical data sets without the absolute consistency necessary to assess spatial and temporal trends.

Terms of Reference (max. 250 words/177)

1. To establish mechanisms to ensure comparability of oceanic nutrient data
2. To assess the homogeneity and stability of currently available RMs/CRMs. It remains to determine whether the current producers are achieving a level of precision within and between laboratories which is comparable to or better than 1 %.
3. To develop standardized data-handling procedures with common data vocabularies and formats, across producers and users, and will 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.
4. To promote the wider global use of RM's by arranging workshops to actively encourage their use and to provide training in analytical protocols and best practice, particularly targeted towards developing countries.
5. To continue regular global inter-comparison studies, following on from the previous exercises in 2003, 2006, 2008 and 2012, with collaboration of IOCCP-SSG and RCGC-JAMSTEC.
6. To update the GO-SHIP nutrient measurement manual, which was originally a product of the IOC-ICES SGONS, (Study Group on Nutrient Standards).
7. To publish reports on this WG's activities and workshops.

Working plan (logical sequence of steps to fulfil terms of reference, with timeline. Max. 1000 words/446)

This Working Group will work 3 years after acceptance by the SCOR General assembly in 2014. The time-line shown below highlights only the main meetings/activities. We will have regular e-mail exchanges, Skype meetings, and a variety of workshops/meetings among the full and associated members that will occur on a regular basis.

Year 1: 2015

Kick-off Meeting: Upon funding, the WG will have a kick-off meeting in early to mid 2015. In order to provide good international visibility, the 2015 EGU General Assembly (April 12-17 2015, Vienna, Austria) is a good potential venue where a WG meeting #1 on changes of nutrients in the world's oceans and use of RMs/CRMs could be held.

Conduct an inter-laboratory comparison experiment of currently available RMs/CRMs by several selected key laboratories to assess the homogeneity and stability of currently available RMs/CRMs. This will be organized by a few of full/associate members of the WG. The results of this will be published as soon as possible after the experiment.

Year 2: 2016

A potential venue for the half-way meeting, WG meeting #2 will be the 2016 Ocean Sciences

Meeting (21 February 2016 — 26 February 2016, New Orleans, Louisiana, USA). During the OSM 2016, we will propose a presentation session at the meeting, and we will also hold a workshop to promote the wider global use of RM's, to actively encourage their use. We will also review synthesis papers and previously published inter laboratory comparison study reports, and prepare a revised version of the GO-SHIP nutrients measurement manual during this workshop. One of key issues is to update/confirm basic analytical methodologies for nitrate, nitrite, phosphate and silicate.

We will conduct a global inter-comparison study of RMs/CRMs following on from the previous exercises in 2003, 2006, 2008, 2012 and 2014, with the collaboration of IOCCP-SSG and RCGC-JAMSTEC.

In 2016 we will provide a training course in analytical methodologies and best practice of nutrient measurement, particularly for developing countries. Potential venues for this training course are NIOZ/The Netherlands, SIO/USA, or JAMSTEC/Japan. In this training course, participants will be given training by experienced analysts and the workshop will discuss the results of the global inter-comparison studies of RMs/CRMs so as to learn more about how to ensure comparability of oceanic nutrient data.

These opportunities, the training course and global inter-comparison study, will also contribute to building capacities in developing countries to measure nutrient concentrations in seawater.

Year 3: 2017

We will plan an international symposium "Towards comparability of global oceanic nutrient data". This symposium is also WG meeting #3. Potential venues for this symposium are JAMSTEC/Japan, NIOZ/The Netherlands and SIO/USA. We will particularly focus on inviting scientists from developing countries, and encourage their involvement in this symposium.

Deliverables (state clearly what products the WG will generate. Should relate to the terms of reference. Max 250/163). A workshop is not a deliverable. Please note that SCOR prefers that publications be in open-access journals.

1. Assessment reports of currently available RMs/CRMs based on inter-laboratory comparison experiments which will be submitted to 'Biogeochemistry' or similar open access journal.
2. A "best practice" manual which will provide the community with a recommended consistent approach to the sampling, analysis, use of RM's, quality control of nutrients, and subsequent data handling which will be an update of the GO-SHIP nutrients manual (Hydes et al 2010).

This manual will be available freely at the GO-SHIP website and will be able to be downloaded free of charge. A printed version of this manual may be published depending on additional funding availability.

3. A report on global inter-comparison studies of RMs/CRMs will be submitted to the journal “Earth System Science Data” published by EGU.
4. Synthesis papers on current nutrient measurements techniques/methodologies which will be submitted to the journal “Earth System Science Data” published by EGU.
5. A book will be published from the final International symposium “Towards comparability of global oceanic nutrient data”.

Capacity Building (How will this WG build long-lasting capacity for practicing and understanding this area of marine science globally.Max500/277

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 involvement and help of POGO. The second is to invite participating laboratories to a 3-day training course in 2016 planned to be held at JAMSTEC/Japan, NIOZ/The Netherlands or SIO/USA (depending on additional funding) to learn more about analytical methodologies, best practice, and to discuss and interpret results of the global 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 even greater participation in the future inter-laboratory comparison study of RM’s proposed for 2016 from these developing countries. 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 requirements, this will all be accomplished with the help and advice of POGO.

The laboratories that took part in the 2012 inter-comparison exercise of nutrients in seawater are already 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. This proposed SCOR WG will endeavor to expand the global participation of developing countries from the current number of 2012/2014 representatives into the 2016 inter-calibration exercise with more participants from developing countries..

Working Group composition (as table). Divide by Full Members (10 people) and Associate Members, taking note of scientific discipline spread, geographical spread, and gender balance. (max. 500 words)

Full Members (no more than 10, please identify chair(s))

Name	Gender	Place of work	Expertise relevant to proposal
1 Michio Aoyama*	Male	RCGC-JAMSTEC/IER-Fukushima Univ., Japan	Geochemistry, global nutrients distribution
2 E. Malcolm S. Woodward*	Male	PML, UK	Nanomolar level precision measurements
3 Toste Tanhua	Male	GEOMAR, Germany,	Chairman of the International Ocean Carbon Coordination Project (IOCCP)
4 Karin Bjorkman	Female	Laboratory for Microbial Oceanography, Hawaii, USA	HOT time series
5 Bernadette Sloyan	Female	CSIRO, Australia	Co-chair of The Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP)
6 Anne Daniel	Female	IFREMER, France	French nutrient reference laboratory (DYNECO/PELAGOS, IFREMER)
7 Susan Becker,	Female	SIO, USA	Repeat Hydrography
8 M. Dileep Kumar	Male	NIO, India	Chemical Oceanography
9 Claire Mahaffey	Female	University of Liverpool, UK	Nutrient Biogeochemist
10 Howard Waldron	Male	University of CapeTown, South Africa	Nitrogen dynamics in Ocean systems

* : Co-Chairs

Associate Member (no more than 10)

Name	Gender	Place of work	Expertise relevant to proposal
1 Alex Kozyr	Male	CIDIAC, USA	Multiple user database access
2 Karel Bakker	Male	NIOZ, The Netherlands	The Netherlands sea-going analytical facility
3 Takeshi Yoshimura	Male	CRIEPI, Japan	Organic Nutrients
4 Jonathan Sharp	Male	University of Delaware, USA	DOC RM experience
5 Andrew Dickson	Male	SIO, USA	Carbonate system RM experiences
6 Minhan Dai	Male	Xiamen University, China	Large global (LOICZ and Chinese programs)
7 Akihiko Murata	Male	JAMSTEC, Japan	Chemical oceanography, Global carbon/nutrient stoichiometry
8 Trevor Platt	Male	PKL, UK	Executive Director, POGO
9 Ralph Sturgeon	Male	NRC, Canada	CRM producer
10 Akiharu Hioki	Male	NMIJ, Japan	CRM producer

Working Group contributions (Max 500/500)

Michio AOYAMA organized the previous 4 Inter-laboratory comparison experiments for Reference Materials of Nutrients in Seawater, RMNS, in 2003, 2006, 2008 and 2012. He is working to develop RMNS, and has been PI of nutrients of 6 CLIVAR cruises in the Pacific Ocean. He is one of PIs of dissolve oxygen and nutrients part of Pacific Ocean Interior Carbon Data Synthesis project, PACIFICA. He has 104 publications in peer-reviewed journals and numerous reports.

Malcolm WOODWARD has worked as a Chemical Oceanographer for 35 years, and Head of the Plymouth Marine Laboratory Nutrients Facility for the past 20 years, has 100 publications in peer-reviewed journals and numerous reports. Has specialized and developed nanomolar nutrient analysis techniques and their applications in global oligotrophic oceans.

Toste TANHUA works on research fields of transient tracers in the ocean, ocean ventilation and mixing, tracer release experiments to quantify mixing. He also conducts CARINA Data Synthesis Project in the Atlantic Ocean. Now he works as a chair of The International Ocean Carbon Coordination Project (IOCCP). He has numerous publications in peer-reviewed journals reports and books.

Karin BJORKMAN works the field of microbial oceanography and nutrient dynamics with a special focus on phosphorus cycling in the oligotrophic North Pacific subtropical gyre. This

work includes high sensitivity measurements low nano-molar concentrations of inorganic phosphate as well as the use of radioisotopes as tracers.

Bernadette SLOYAN works on International repeat hydrography and carbon program. She analyzes repeat hydrographic sections in the southern hemisphere oceans and simulation of deep ocean changes in climate models. She has numerous publications in peer-reviewed journals reports and books.

Anne DANIEL is in charge of the French reference laboratory (DYNECO/PELAGOS, IFREMER) for chemical measurement in marine and fresh waters. It supports laboratories by developing new methodologies, organizing performance tests and implementing quality system for accreditation according to the ISO/IEC 17025 norm. She also works in the implementation of the EU Water Framework Directive (WFD) and EU Marine Water Framework Directive (MSFD).

Susan BECKER is a manager and supervisor for the Oceanographic Data Facility within Shipboard Technical Support at Scripps Institution of Oceanography. She is responsible for overseeing the analytical analysis and data quality of inorganic nutrients, dissolved oxygen, and salinity. ODF provides the highest quality hydrographic data from CTD casts and discreet analysis of salinity, nutrients and dissolved oxygen for global repeat hydrography programs.

M. Dileep KUMAR is a Chemical Oceanographer focusing on nutrient and carbon biogeochemistry with particular reference to Climate Change. He has about 35 years of research experience at NIO (Goa) and has about 65 publications in peer-reviewed journals.

Claire Mahaffey is a nutrient biogeochemist and Senior Lecturer with over 10 years experience studying the source, cycling and fate of nitrogen, phosphorus and carbon in the subtropical open ocean and coastal and shelf seas. Has been responsible for nutrient analysis both at the Hawaii Ocean Time Series (USA) and Liverpool Bay Coastal Observatory (UK).

Howard WALDRON works on nitrogen dynamics of ocean systems including Benguela Upwelling, Southern Ocean and Atlantic Meridional Transect.

Relationship to other International programs and SCOR Working groups (max. 500 words/78)

Toste Tanhua is a Chair of The International Ocean Carbon Coordination Project (IOCCP).

Bernadette Sloyan is a Co-chair of The Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP).

Trevor Platt is an Executive Director of the Partnership for Observation of the Global Oceans

(POGO).

Michio Aoyama is a candidate of full member of SCOR WG proposal of marine radioactivity which will be submitted in 2014. Minhan Dai is also a candidate of co-chair of SCOR WG proposal of marine radioactivity.

Key References (Max. 500/497)

- Aoyama, M. et al. (2007) Recent comparability of Oceanographic Nutrients Data: Results of a 2003 Intercomparison Exercise using Reference Materials, *Anal. Sci.* 23, 1151-1154.
- Aoyama, M. et al. (2008) 2006 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix, Technical Reports of the Meteorological Research Institute No. 58.
- Aoyama, M. et al. (2010) 2008 Intercomparison Exercise for Reference Material for Nutrients in Seawater in a Seawater Matrix, Technical Reports of the Meteorological Research Institute No. 60.
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- Wanninkhof, R. et al., (2010), Detecting anthropogenic CO₂ changes in the interior Atlantic Ocean between 1989 and 2005. *Journal of Geophysical Research*, 115, C11028, doi:10.1029/2010JC006251.

Appendix

For each Full Member, indicate 5 key publications related to the proposal.

Michio Aoyama

Aoyama, M., Ota, H., Kimura, M., Kitao, T., Mitsuda, H., Murata, A., and Sato, K.: (2012). Current Status of Homogeneity and Stability of the Reference Materials for Nutrients in Seawater, *Analytical Sciences*, 28, 911-916. DOI: 10.2116/analsci.28.911.

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Aoyama, M., C. Anstey, J. Barwell-Clarke, F. Baurand, S. Becker, M. Blum, S. C. Coverly, E. Czobik, F. D'amico, I. Dahllof, M. H. Dai, J. Dobson, M. Duval, C. Engelke, G. C. Gong, O. Grosso, A Hirayama, H. Inoue, Y. Ishida, D. J. Hydes, H. Kasai, R. Kerouel, M. Knockaert, N. Kress, K. A. Kroglund, M. Kumagai, S. C. Leterme, C. Mahaffey, H. Mitsuda, P. Morin, T. Moutin, D. Munaron, A. Murata, G. Nausch, H. Ogawa, J. van Ooijen, J. M. Pan, G. Paradis, C. Payne, O Pierre-Duplessix, G. Prove, P. Raimbault, M. Rose, K. Saito, H. Saito, K. Sato, C. Schmidt, M. Schutt, T. M. Shammon, S. Olafsdottir, J. Sun, T. Tanhua, S. Weigelt-Krenz, L. White, E. M. S. Woodward, P. Worsfold, T. Yoshimura, A. Youenou, J. Z. Zhang (2010). 2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater. *Technical Reports of the Meteorological Research Institute*, 60, 1-134.

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Malcolm Woodward

Browning, T. J., Bouman, H. A., Moore, C. M., Schlosser, C., Tarran, G. A., **Woodward, E. M. S.**, and Henderson, G. M.: (2014): Nutrient regimes control phytoplankton ecophysiology in the South Atlantic, *Biogeosciences*, 11, 463-479, doi:10.5194/bg-11-463-2014, 2014

Christian Schlosser, Jessica K Klar , Bronwyn Wake , Joe Snow , David Honey , **E. Malcolm S. Woodward** , Maeve Lohan , Eric P. Achterberg , C. Mark Moore (2013). Seasonal ITCZ migration dynamically controls the location of the (sub-)tropical Atlantic biogeochemical divide. *Proceedings of the National Academy of Sciences*. 12/2013; DOI:10.1073/pnas.1318670111

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Toste Tanhua

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Tanhua, T., Brown, P., Key, R. M., 2009. CARINA: nutrient data in the Atlantic Ocean, Earth System Science Data, 1, 7-24.

Karin Bjorkman

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