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Comparability of Oceanic nutrient data

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Abstract

To allow the global community to be able to accurately and confidently detect and quantify changes in oceanic nutrient concentrations now, and in the future, it is important to establish mechanisms for improving the quality of reported oceanic nutrient data. The SCOR WG#147 “Towards comparability of global oceanic nutrient data”, has been established to encourage the use of certified nutrient reference materials, and to advise on improvements to the analysis of nutrients in laboratories globally. For future generations it is now unacceptable to produce data sets without the consistency necessary to assess spatial and temporal trends and variability, potentially caused by human impacts, such as climate induced changes in ocean circulation and productivity/remineralisation Improved comparability of reported nutrient concentrations in the water column will also facilitate improved estimates of the anthropogenic carbon in the water column.

1. Introduction

Global oceanic biogeochemical cycles are being significantly altered by the direct and indirect impacts of human activities. It is therefore necessary to obtain accurate observations of changes and trends in carbon and dissolved nutrients, in both upper and deep ocean waters. For these accurate observations, it is critical that we can reliably compare results from different laboratories, for geographically similar ocean waters, with complete confidence. To get a global consensus for nutrient data, it is necessary to have access to accepted certified reference materials (CRMs), and to encourage and establish a requirement or ethos for the use of these CRMs when analyzing for oceanic nutrient concentrations, and subsequently for reporting these values to global databases, and then for use in climate models, and to ultimately observe and quantify changes to the earth system.

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).

2. Identify key research gaps and opportunities to address the motivating questions and challenges

The 2007 IPCC Report highlighted the problem inherent in comparing data sets by 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). Analysis of nutrient concentrations from crossover stations (secondary quality control) have shown biases of up to 10 % for deep nutrient data during the last three decades (Aoyama et al., 2013, Tanhua et al., 2009). Similarly results of inter-laboratory comparison studies since 2003 have showed a similar magnitude of bias among some participant laboratories (Aoyama et al., 2007; 2008; 2010). This indicates that analytical problems may be the main cause of the large discrepancies in reported deep water nutrient concentrations (implying that these biases are also present throughout the water column according to the reported results). These comparisons were from only 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 total confidence, any temporal changes in oceanic nutrient concentrations. 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) due to the comparability of temperature measurements over a number of years. 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). Similarly, changes to oceanic oxygen can now also be accurately observed (Stendardo and Gruber, 2012).

Highlighting the need for improvements in nutrient data comparisons made by the activity of this SCOR working group, in collaboration with IOCCP and JAMSTEC, and through global nutrient inter-comparison studies (Aoyama et al., 2016), the process of awareness through the global community has continued. International projects like GEOTRACES are instrumental in establishing data quality protocols for accepting data, as they specify CRM usage and result reporting as part of their data submission process. The nutrients submitted to the GEOTRACES database are subject to rigorous scrutiny and checking against reference materials by a data committee, and by comparisons to other laboratory data reported from cross-over stations from different cruises on different days. This not only encourages laboratories to use reference materials but also encourages individual laboratories to check and improve their analytical and sampling methods, knowing that their data will come under close scrutiny by independent scientists before being accepted into the GEOTRACES database.

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 CRMs, followed by the recommendation of protocols (best practice guidelines) for their use throughout the world-wide marine chemistry community. This has already been achieved for other parameters like salinity and CO_2. A potential solution in encouraging 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 needs to be established so as laboratories routinely adopt RM/CRMs into their regular protocols. There was significant improvement in the DOC measurements during the international JGOFS program due to encouragement by the US National Science Foundation and NOAA for laboratories to participate in DOC comparability exercises (Sharp et al, 2002).

The SCOR WG#147 will provide the authority for not only certification of nutrient

CRMs, but also establish protocols for their use, and install a system that can be used after the end of the WG. Previously, 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 also 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”.

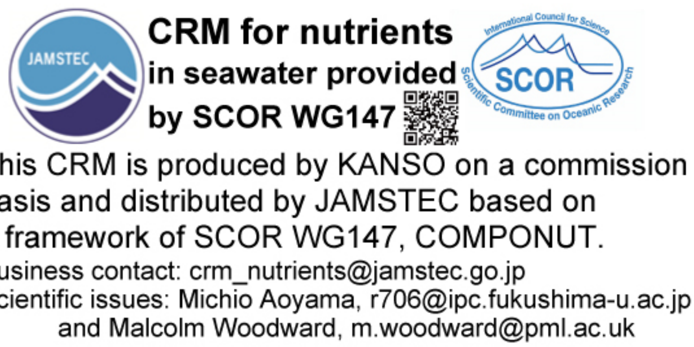
Since that time, RMs/CRMs for oceanographic use have been developed. These currently include a Danish RM (Eurofins), NRC-Canada CRM (MOOS-3), a new RM development by Korea (K-RMS), and one developed by KANSO-Japan. A comparison of these materials was carried out as part of the 2015 International nutrient comparison exercise (Aoyama et al 2016).

Therefore, we will now have the opportunity for traceability and comparability of nutrient concentrations throughout the global oceans by encouraging the use of these available CRM’s, and a mechanism to provide RMs that are traceable to SI (International System of Units) through CRMs.

Through the encouragement and activities of this SCOR WG#147, the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) will start to provide a range of certified reference material (CRM) appropriate for Nitrate, Nitrite, Silicate and Phosphate nutrient concentrations found in the Pacific and Atlantic Oceans, on 1st

September 2016. This will give seawater nutrient scientists a number of options for their own specific analytical needs when analyzing oceanic samples for nutrients.

These CRM's will be produced on a commission basis by the Japanese producer KANSO, who have many years' experience in nutrient CRM production. The CRM's will be sold and distributed by JAMSTEC though the framework established by the SCOR WG#147. There will be a new low cost-structure for the CRM's being sold by JAMSTEC and this new lower pricing should encourage and enable their use by more laboratories. (see label and a photo of new CRM sample bottle below).



SCOR WG#147 "Towards comparability of global oceanic nutrient data (COMPONUT) (http://www.scor-int.org/SCOR_WGs_WG147.htm).

3. Present status of comparability: Results from IOCCP-JAMSTEC 2015 Inter-laboratory Calibration Exercise of a Certified Reference Material for Nutrients in Seawater

The results off the "IOCCP-JAMSTEC 2015 Inter-laboratory Calibration Exercise of a Certified Reference Material for Nutrients in Seawater" (http://www.scor-int.org/SCOR_WGs_WG147.htm) are now available (Aoyama et al 2016). From the current results (see for example Fig 1. below for Nitrate) it is clear that comparability among the participants in the 2015 I/C exercise is similar to those achieved with previously obtained comparability in 2012 and earlier (Aoyama et al., 2007; 2008; 2010; 2013). Consensus standard deviations of all determinands are one order of magnitude larger when compared to the homogeneity of the CRMs that were distributed for analysis, and are about double the reported precision of measurements of the individual laboratories. Therefore these I/C results show that use of CRM should be able to greatly improve comparability of nutrient data among the laboratories across the world by reducing the magnitude of those standard deviations.

However, there are encouraging outcomes from the results. Although consensus standard deviations are relatively large, the consensus median/mean of each sample showed good agreement with certified values of the samples, and were within consensus standard deviations. This implies that the majority of the participating laboratories actually do have a capability to accurately measure nutrient concentrations in seawater, but that by using CRM's regularly it will improve their comparability and move towards being SI traceable.

Thus, the use of a common reference material, the adoption of an internationally agreed-upon nutrient scaling system, and the common use of the methodology of nutrients measurements would improve comparability among laboratories worldwide. The use of a certified reference material would establish traceability, based on the current high level of analytical performance at many participating laboratories.

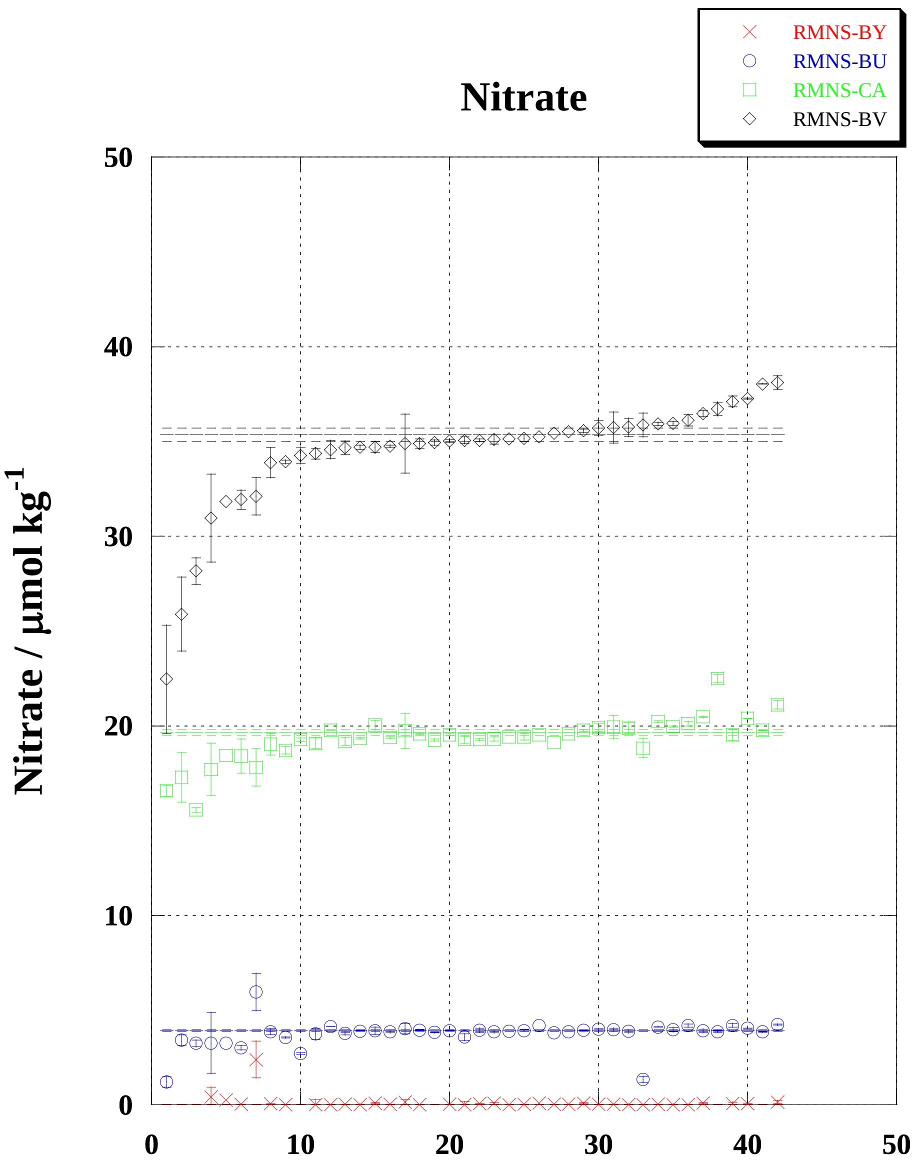


Figure 1. Nitrate results for KANSO CRMs. Laboratories are ranked in order of concentrations reported for RM-BV (from Figure 2-1 in the report of 2015 I/C exercise at http://www.scor-int.org/SCOR_WGs_WG147.htm)

4. Traceability and comparability of reported nutrient concentrations throughout the global ocean, for the long-term study of biogeochemical changes in the marine environment

One of the objectives of CLIVAR is to describe and understand the dynamics of the coupled ocean-atmosphere system and to identify processes responsible for climate variability, change and predictability on seasonal, inter-annual, decadal, and centennial time-scales. This is through the collection and analysis of observations, and the development and application of models of the coupled climate system, in cooperation with other relevant climate-research and observing activities. (http://www.clivar.org/about/about-clivar).

For the scientific biogeochemical study of the marine environment, we need an international hydrography program that has a sustained protocol for coordination of data and information management, and for data synthesis activities. In such an international hydrography program, there would be the requirement for traceability and comparability of nutrient concentrations throughout the globe, and for this to continue into the future. This will include the seasonal, inter-annual, decadal, and centennial time-scales, and so will enable us to describe and understand the dynamics of any biogeochemical changes, and to identify processes responsible for climate variability through changes in the concentrations of nutrients and inorganic carbon.

SCOR WG#147 will establish the mechanisms required to provide comparability of oceanic nutrient data.

The major challenge for this SCOR WG#147 is to develop a system by which the comparability of data within and between laboratories is at or better than 1% of full scale of nitrate, phosphate and silicate concentrations. The current levels of comparability achieved for the measurement of oceanic salinity and total inorganic carbon are already considerably better than 1%. However, both of these parameters are comparatively chemically simple, and exist in the open ocean in much narrower concentration ranges than inorganic nutrients, that may span orders of magnitude across the global oceans.

5. Conclusion

The primary goal for the SCOR WG#147 is to put in place mechanisms and recommendations to ensure that nutrient data collected at any one place by an individual laboratory, will be consistent and traceable through the use of certified reference materials so that data produced by one or more laboratories can be compared over long time periods. Programme and laboratory managers must invest in staff skills and training to ensure that the analytical nutrient data output is supported financially and technically in order to produce comparable data using reference materials and by adhering to the sampling and analytical recommendations of the GO-SHIP nutrient manual (Hydes et al 2010, Becker et al., 2017). The experience of this SCOR WG#147 will also give positive feed-back to the scientific community of coastal ocean observatories, and for researchers developing nutrient sensors for buoys, gliders and floats, by providing and recommending globally accepted RMs/CRMs for the calibration of instruments and sensors.

Such feedback will move toward the global goal of achieving comparability of nutrient data throughout the global oceans, which will have been obtained by different methods, instruments, and technologies.

This SCOR initiative is based on a previously developed international laboratory collaboration, set up within IOC-ICES SGONS (Study Group on Nutrient Studies) that ended in 2012.

For future generations it is unacceptable to produce nutrient data sets without the absolute consistency necessary to assess spatial and temporal trends.

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