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Contents

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Abstract

A meeting of the joint IOC-ICES Study Group on Nutrient Standards (SGONS) was held in Paris, France, on 23–24 March 2010. It focused on the ongoing activities of the SGONS and plans for extended international collaborations to establish global comparability of the nutrient data from the world's ocean. Thirty two scientists and experts from 11 countries and 2 delegates from IOC attended the meeting. The discussions followed the Terms of References of SGONS established in July 2009. Development of the reference materials for nutrients in seawater (RMNS) were also discussed in collaboration with the producers. The background and history of SGONS and an international nutrients scale system INSS and the progress with the production of RMNS materials and their current availability were reported. The production of RMNS and the latest status of the RMNS production facility, current status on the certification of RMNS for nitrate, nitrite, phosphate and silicate at the National Metrology Institute of Japan were also reported. The revised nutrients analysis manual which is being undertaken by the SGONS hopefully would be completed by 1 August 2010, and it will be published on line at the Go-Ship website. Results obtained with RMNS solutions used on the P6 reoccupation cruise in 2009/2010 by SIO (Scripps Institute of Oceanography, USA) showed that considerable improvement could be made in the internal comparability of the data by referencing it to the RMNS results and related good comparability with the previous P6 cruise in 2003 by JAMSTEC when RMNS were also used. The meeting strongly endorsed the idea of a ship board workshop in 2013/2014 during which major groups would carry out a full intercomparison of all procedures including analytical methods on board a research ship. The global stability test of RMNS by ten core laboratories of SGONS which started in 2009 will continue for more two years. It also was agreed to set up an international steering committee to plan the next inter-laboratory comparison study which will extend the study to about 70 laboratories working globally on deep sea hydrography. This will happen in early 2011. Future arrangements were considered for the collection of more batches of seawater for the preparation of RMNS waters suitable for use in all major water masses, and a list of candidate cruises in 2010/2011 was prepared. The related point of the extension of the use of RMNS for work in shelf sea water was also discussed, this followed on from discussions at the ICES Marine Chemistry Working Group (MCWG) meeting in 2010. The ICES MCWG considered that the use of suitable RMNS solutions would be valuable for improving the inter comparability of shelf sea data and be a valuable complement to work with the existing QUASIMEME proficiency testing scheme.

*This document contains an executive summary in English, French, Spanish and Russian.

Executive summary

A meeting of the joint IOC-ICES Study Group on Nutrient Standards (SGONS) was held in Paris, France, on 23–24 March 2010. It focused on the ongoing activity of SGONS and plans for extended international collaborations to establish global comparability of the nutrient data from the world's ocean. Thirty-two scientists and experts from 11 countries and 2 delegates from IOC attended the meeting.

Presently the basic problem when comparing data for concentrations of nutrients in the ocean is that when data from different cruises are compared at cross over points the comparability is not as good as was hoped for when methods were review by the WOCE planning groups in 1993. Rather than the 1% comparability expected, cross over comparisons may be several percent out.

Recent RMNS inter comparison studies in 2003, 2006 and 2008 have found agreement close to what WOCE considered possible for the better laboratories, while the 2008 exercise also showed indications of number of systematic errors in some of the results. These inter-comparison studies have been valuable in spreading awareness of the materials and a further exercise is to be planned for early 2011 which will be expanded to 70 laboratories primarily working in the deep sea.

Important lessons can be learnt from this effort in demonstrating what meta data needs to accompany nutrient data when it is logged in a databank. The need for establishing good meta data reporting practice alongside the use of RMNS was discussed throughout the meeting. Therefore we will prepare a standard form for meta data reporting for future cruises and inter comparison studies.

National Metrology Institute of Japan, NMIJ, is certifying three levels of Reference material for nutrients in seawater (RMNS) for nitrate, nitrite, phosphate and silicate nutrient seawater – extreme low concentration, middle concentration and high concentration. Low and high concentration water has already been collected. It was agreed to collect and provide seawater in 2010 to produce/certify middle level of certified RMNS using Atlantic deep water.

The preparation of the revised nutrients analysis manual which is being undertaken by the SGONS was reported. It was agree to complete the revised manual including SOPs by 1 August 2010. It will be published on line by Go-Ship. A definitive publisher of the manual such as IOC or ICES needs to be found.

The meeting strongly endorsed the idea of a ship board workshop in 2013/2014 during which major groups would carry out a full inter-comparison of all procedures including analytical methods on board a research ship.

Results obtained with RMNS solutions used on the P6 reoccupation cruise in 2009–2010 by Scripps Institution of Oceanography (SIO) were reported. The report showed that considerable improvements could be made in the internal comparability of the data and comparability with the previous P6 cruise in 2003 by Japan Agency for Marine-Earth Science and Technology (JAMSTEC) when RMNS were also used.

Figures of the results of the global stability test by ten core laboratories were shown for nitrate, phosphate and silicate. With the exception of the JAMATEC data, the data presented were not consistent as expected. The reasons for this need are to be investigated. The JAMSTEC data however seems to suggest that the RMNS are stable for the time period analyzed so far.

Developing reference materials for dissolved organic matter was reported. The results of a test on RMNS for dissolved organic matters showed that RMNS was not good for dissolved organic matter. Further work is planned.

Development of a non-toxic RM of the carbonate systems was reported. This is needed to support the growth in demand for such solutions for work on ocean acidification. Quality control of seawater pH is indispensible for the evaluation of ocean acidification, therefore we intend to develop reference material for pH. Three candidates for RM for seawater pH are as follows; existing toxic RM, which is already certified for DIC and TA. non-toxic RM and Tris buffer.

The related point of the extension of the use of RMNS for work in shelf sea water was also discussed, this followed on from discussions at the ICES Marine Chemistry Working Group (MCWG) meeting on 2010. The ICES MCWG considered that the use of suitable RMNS solutions would be valuable for improving the inter comparability of shelf sea data and be a valuable complement to work with the existing Quality Assurance of Information in Marine Environmental Monitoring in Europe (QUASIMEME) proficiency testing scheme. The Paris meeting then discussed the possible need for a further global inter-comparison exercise for laboratories working mainly in shelf seas. This would complement the planned 2011 exercise, which would focus on laboratories whose main concern was deep ocean waters.

At the 2010 Paris meeting of the joint IOC-ICES SGONS, all participants recognized the need to establish comparability of nutrients data in the world ocean through International Nutrients Scale System, INSS, and build more international collaborations for this goal. In particular, the meeting participants (1) agreed a further inter comparison studies of RMNS for early 2011 which will be expanded to 70 laboratories primarily working in the deep sea, (2) prepare a form for meta data report of nutrients measurements for cruises and inter comparison studies, (3) keep collaboration with NMIJ and collect/provide seawater in 2010 to produce/certify middle level of certified RMNS using Atlantic deep water, (4) continue the global stability test of RMNS by ten core laboratories until October 2011, (5) complete the revised nutrients analysis manual including SOPs by 1 August 2010. It will be published on line by GoShip, (6) continue development of reference materials for dissolved organic matters, (7) continue development of non-toxic RM of the carbonate systems especially for non-toxic RM of pH. RMs are needed to support the growth in demand for such solutions for work on ocean acidification.

Addition presentation at the meeting covered: (1) a comparison study carried out in the Baltic that showed a high degree of comparability in the data collected on three ships when trained workers used sampling and storage bottles of the same design and followed the same procedures; (2) methods developed by IFREMER which reduce problem of interference when measuring samples of different salinity on an autoanalyser; (3) measurements of oxygen using fast-responding optode sensors and the latest results of a feasibility study for RM for dissolved oxygen.

Résumé

Le Groupe d'étude conjoint COI-CIEM sur les normes en matière de nutriments (SGONS) s'est réuni à Paris (France) les 23 et 24 mars 2010. La réunion a porté sur les activités en cours du SGONS et les projets de collaborations internationales étendues visant à comparer, au niveau mondial, les données relatives aux nutriments dans tous les océans du monde. Ont participé à la réunion, 32 scientifiques et experts venant de 11 pays et deux représentants de la COI.

À l'heure actuelle, le problème essentiel que pose la comparaison de données relatives aux concentrations de nutriments dans l'océan tient au fait que la comparabilité des données issues de différentes campagnes et rapprochées transversalement n'est pas aussi bonne que ne le laissait espérer la révision des méthodes par les groupes de planification de la WOCE en 1993. Loin du 1 % de comparabilité attendu, les comparaisons transversales peuvent varier de plusieurs points de pourcentage.

Les résultats de récentes études d'intercomparaison des Matériels de référence pour les nutriments dans l'eau de mer (RMNS), menées en 2003, 2006 et 2008, rejoignent ce que la WOCE considérait faisable pour les meilleurs laboratoires, l'exercice de 2008 faisant également état d'un certain nombre d'erreurs systématiques dans plusieurs résultats. Ces études ont été précieuses pour faire connaître lesdits matériels et une nouvelle étude, prévue pour début 2011, sera étendue à 70 laboratoires travaillant essentiellement en eau profonde.

Il y a beaucoup à apprendre de cet effort visant à établir quelles métadonnées doivent être associées aux données relatives aux nutriments quand celles-ci sont consignées dans une base de données. La nécessité d'établir de bonnes pratiques de transmission des métadonnées, parallèlement à l'utilisation des RMNS, a été évoquée tout au long de la réunion. Nous mettrons donc au point un formulaire type pour la transmission des métadonnées à l'intention des futures campagnes et études d'intercomparaison.
L'Institut national de métrologie du Japon (NMIJ) certifie trois niveaux de RMNS pour les nitrates, les nitrites, les phosphates et les silicates : très faible concentration, concentration moyenne et concentration élevée. De l'eau contenant des concentrations faibles et élevées a déjà été collectée. Il a été convenu qu'en 2010, de l'eau de mer serait collectée/fournie pour établir/certifier le niveau moyen de RMNS certifiés, en utilisant de l'eau provenant des fonds de l'Atlantique.

Il a également été fait état de la préparation de la version révisée du manuel d'analyse des nutriments, actuellement conduite par le SGONS. Il a été convenu que cette version comprendrait les procédures opérationnelles normalisées et serait achevée avant le 1er août 2010. Elle sera publiée en ligne par GO_SHIP. Il reste à trouver un éditeur définitif pour le manuel, tel que la COI ou le CIEM.

Le Groupe d'étude a fermement soutenu l'idée d'un atelier à bord d'un navire en 2013–2014, ce qui permettrait aux principaux groupes de mener des études intercomparatives complètes de toutes les procédures, y compris les méthodes d'analyse, à bord d'un navire de recherche.

Le Groupe était saisi d'un rapport portant sur les résultats obtenus grâces aux solutions de RMNS utilisées lors de la campagne de réoccupation P6 conduite par l'Institut Scripps d'océanographie (SIO) en 2009/2010. Il en ressort que l'on pourrait considérablement améliorer tant la comparabilité interne des données que la comparabilité avec la précédente campagne P6 conduite en 2003 par l'Agence japonaise

pour la science et la technologie marine et terrestre (JAMSTEC), au cours de laquelle des RMNS ont également été employés.

Les résultats chiffrés des tests de stabilité globale réalisés par 10 laboratoires cléfs ont été présentés pour les nitrates, les phosphates et les silicates. Les données, à l'exception de celles de la JAMSTEC, ne présentaient pas la régularité attendue, et il faut en déterminer les causes. Cela dit, les données de la JAMSTEC semblent suggérer que les RMNS sont stables pour la période analysée jusqu'à présent.

Les matériels de référence pour les matières organiques dissoutes, actuellement mis au point, ont été évoqués. Les résultats d'un test de RMNS pour matières organiques dissoutes ont révélé que les RMNS n'étaient pas appropriés pour ces matières. Des études complémentaires sont prévues.

Le développement d'un matériel de référence non toxique du système des carbonates a été présenté. Ce matériel est nécessaire afin de répondre à la demande accrue de telles solutions pour les travaux sur l'acidification de l'océan. Un contrôle de qualité du pH de l'eau de mer étant indispensable à l'évaluation de l'acidification de l'océan, nous nous proposons de mettre au point un matériel de référence pour le pH. Trois matériels de référence sont envisagés pour le pH de l'eau de mer : le matériel de référence toxique existant, déjà certifié pour le carbone inorganique dissout et l'alcalinité totale, le matériel de référence non toxique et le tampon Tris.

La question connexe de l'extension de l'usage des RMNS aux travaux en eaux de mer épicontinentale a également été débattue, suite aux échanges à ce sujet lors de la réunion de 2010 du Groupe de travail du CIEM sur la chimie marine (MCWG). Ce groupe avait alors considéré que l'usage de solutions de RMNS adaptées aiderait à améliorer l'intercomparabilité des données relatives aux mers épicontinentales et représenterait un complément appréciable aux essais d'aptitude existants réalisés par QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring in Europe). Le SGONS, réuni à Paris, a donc étudié la nécessité d'un nouvel exercice d'intercomparaison global pour les laboratoires travaillant essentiellement dans les mers épicontinentales. Celui-ci viendrait en complément de l'exercice prévu en 2011, qui sera consacré aux laboratoires s'occupant principalement des eaux profondes.

Lors de la réunion de 2010 à Paris du Groupe d'étude conjoint COI-CIEM sur les normes en matière de nutriments, tous les participants ont reconnu la nécessité d'établir la comparabilité des données relatives aux nutriments dans tous les océans du monde au moyen de l'Échelle internationale des nutriments (INSS), et d'instaurer à cette fin des collaborations internationales élargies. Ils ont notamment convenu : (1) de réaliser une nouvelle étude d'intercomparaison des RMNS début 2011, qui sera étendue à 70 laboratoires travaillant essentiellement en eau profonde, (2) de préparer un formulaire pour la transmission des métadonnées sur les mesures de nutriments, à l'intention des campagnes et des études d'intercomparaison, (3) de maintenir la collaboration avec le NMIJ et de collecter/fournir de l'eau de mer en 2010 pour établir/certifier le niveau moyen de RMNS certifiés, en utilisant de l'eau provenant des fonds de l'Atlantique, (4) de poursuivre les tests de stabilité globale des RMNS conduits par 10 laboratoires clés jusqu'en octobre 2011, (5) d'achever, avant le 1er août 2010, la version révisée du manuel d'analyse des nutriments, en y incluant les procédures opérationnelles normalisées, et de la faire publier en ligne par GO_SHIP, (6) de poursuivre la mise au point de matériels de référence pour les matières organiques dissoutes, (7) de poursuivre le développement d'un matériel de référence non toxique du système des carbonates, particulièrement d'un matériel de référence non toxique

pour le pH. Ces matériels sont nécessaires afin de répondre à la demande croissante de telles solutions pour les travaux sur l'acidification de l'océan.

Les présentations complémentaires lors de la réunion ont porté sur : (1) une étude comparative menée dans la Baltique, qui a révélé un haut degré de comparabilité entre les données collectées par trois navires différents, quand du personnel qualifié a employé, pour l'échantillonnage et la conservation, des récipients de conception identique et suivi les mêmes procédures, (2) les méthodes développées par l'IFREMER réduisant les problèmes d'interférence dans la mesure d'échantillons de salinité différente avec un autoanalyseur, (3) la mesure de l'oxygène grâce à des capteurs à électrode optique à réponse rapide et les derniers résultats de l'étude de faisabilité concernant les matériels de référence pour l'oxygène dissout.

Resumen dispositivo

Los días 23 y 24 de marzo de 2010 se celebró en París, Francia, una reunión del Grupo de estudio mixto COI-CIEM sobre normas relativas a nutrientes. La reunión estuvo dedicada a la actividad actual del Grupo de estudio y a los planes para ampliar la colaboración internacional con el fin de establecer la comparabilidad mundial de los datos sobre nutrientes obtenidos del océano mundial. A la reunión asistieron 32 científicos y expertos de 11 países, más dos delegados de la COI.

En la actualidad, el problema básico que plantea la comparación de datos de concentración de nutrientes en el océano radica en que, cuando se comparan los datos obtenidos de dos cruceros diferentes en el punto de intersección, la comparabilidad no es tan satisfactoria como se esperaba cuando los grupos de planificación del Experimento de Circulación Mundial de los Océanos examinaron los métodos en 1993. En lugar del 1% de comparabilidad esperado, las comparaciones en los puntos de cruce pueden diferir en varias unidades porcentuales.

Recientes estudios de intercomparación de materiales de referencia respecto de nutrientes de agua de mar (MRNM) efectuados en 2003, 2006 y 2008 han evidenciado un grado de concordancia cercano al que el Experimento de Circulación Mundial de los Océanos consideraba posible en los mejores laboratorios, mientras que el ejercicio de 2008 evidenciaba también errores sistemáticos en algunos de los resultados. Estos estudios han ayudado a difundir el conocimiento de los materiales, y para comienzos de 2011 está previsto un nuevo ejercicio, que se ampliará hasta abarcar 70 laboratorios principalmente especializados en aguas profundas.

De esta iniciativa cabe extraer importantes enseñanzas, que indican los tipos de metadatos que deberían acompañar los datos sobre nutrientes al acceder a un banco de datos. En el transcurso de la reunión se abordó la necesidad de establecer una práctica adecuada para la comunicación de metadatos conjuntamente con la utilización de MRNM. Por ello, elaboraremos un formulario tipificado para la comunicación de metadatos en los cruceros y estudios de intercomparación futuros.

El Instituto Nacional de Metrología de Japón certifica tres niveles de material de referencia para nutrientes de agua marina (MRNM) respecto de nitratos, nitritos, fosfatos y silicatos: concentraciones extremadamente bajas, concentraciones medias, y concentraciones altas. Se ha recogido ya agua de concentración baja y alta. Se acordó recoger y proporcionar en 2010 agua de mar para producir/certificar MRNM de nivel medio con aguas profundas del Atlántico.

Se dio a conocer la preparación de un manual revisado para el análisis de nutrientes, que ha emprendido el Grupo de estudio. Se acordó que la versión revisada, incluidos los procedimientos operativos estándar, quedasen finalizados el 1º de agosto de 2010. El manual será publicado en línea por Go-Ship. Se necesita encontrar una organización que publique la versión definitiva (por ejemplo, la COI o el CIEM).

En la reunión se respaldó decididamente la idea de celebrar en 2013-2014 un taller a bordo de un buque, que permitiría a los principales grupos realizar una intercomparación exhaustiva de todos los procedimientos, incluidos los métodos analíticos utilizados a bordo de los buques de investigación.

Se comunicaron los resultados obtenidos en 2009/2010 por el crucero de reocupación P6 del Scripps Institution of Oceanography (SIO) con soluciones de MRNM. El informe reveló que era posible mejorar considerablemente la comparabilidad interna de

los datos y la comparabilidad con el crucero P6 precedente, que emprendió en 2003 el Centro Marino Japonés de Ciencia y Tecnología de Japón, y en el que se utilizaron también MRNM.

Se indicaron los resultados de la prueba mundial de estabilidad efectuada por 10 laboratorios básicos respecto de nitratos, fosfatos y silicatos. Con la excepción de los datos del Centro Marino Japonés de Ciencia y Tecnología, el resto de los datos presentados no exhibían la coherencia esperada. Será necesario investigar las razones de ese resultado. Sin embargo, los datos del Centro Marino Japonés de Ciencia y Tecnología parecen indicar que los MRNM son estables durante el periodo de tiempo analizado hasta la fecha.

Se comunicó el desarrollo de materiales de referencia respecto de materia orgánica disuelta. Los resultados de una prueba con MRNM respecto de materia orgánica disuelta evidenciaron que los MRNM no eran adecuados para ese tipo de sustancias. Se prevé seguir investigando.

Se informó del desarrollo de un material de referencia no tóxico para los sistemas carbonatados. Este tipo de material es necesario, dado el crecimiento de la demanda de ese tipo de soluciones para el estudio de la acidificación del océano. A tal efecto, es indispensable un control de calidad del pH del agua marina, por lo que nos proponemos desarrollar materiales de referencia para el pH. A ese respecto hay tres candidatos: los materiales de referencia actuales, tóxicos, que han sido ya certificados respecto del carbono inorgánico disuelto y de la acidez titratable; materiales de referencia no tóxicos; y tampones Tris.

A este respecto, se debatió también la posibilidad de utilizar tampones Tris en las investigaciones realizadas sobre la plataforma marina, a raíz de los debates de la reunión del Grupo de trabajo sobre química marina del CIEM, celebrada en 2010. Este Grupo de trabajo consideró que la utilización de soluciones apropiadas de MRNM sería útil para mejorar la intercomparabilidad de los datos de la plataforma marina, y sería asimismo un valioso complemento de las investigaciones basadas en las pruebas de efectividad de 2010 (aseguramiento de la calidad de la información para monitorizar el medio ambiente marino en Europa). En la reunión de París se abordó seguidamente la posible necesidad de un nuevo ejercicio mundial de intercomparación para laboratorios que operan principalmente en aguas de la plataforma marina. Se complementaría así el ejercicio previsto para 2011, que protagonizarían los laboratorios dedicados principalmente al estudio de las aguas profundas del océano.

En la reunión de 2010 del Grupo de estudio mixto COI-CIEM sobre normas relativas a nutrientes, que se celebró en París, todos los participantes reconocieron la necesidad de establecer la comparabilidad de los datos sobre nutrientes en el océano mundial mediante la escala internacional de nutrientes (INSS), y de redoblar la colaboración internacional a tal efecto. En particular, los participantes en la reunión acordaron 1) realizar a comienzos de 2011 un nuevo estudio de intercomparación de MRNM que, en esa ocasión, abarcará 70 laboratorios dedicados principalmente al estudio de las aguas marinas profundas; 2) confeccionar un formulario para la comunicación de metadatos respecto de las mediciones de nutrientes obtenidas de cruceros y estudios de intercomparación; 3) mantener la colaboración con el Instituto Nacional de Meteorología de Japón y recoger/proporcionar agua marina en 2010 con objeto de producir/certificar MRNM de nivel medio con aguas profundas del Atlántico; 4) seguir realizando la prueba mundial de estabilidad de MRNM en tres laboratorios básicos hasta octubre de 2011; 5) finalizar, no más tarde del 1º de agosto de 2010, la versión revisada del manual sobre análisis de nutrientes, incluidos los procedimientos operativos es-

tándar, que será publicada en línea por Go-Ship; 6) seguir desarrollando materiales de referencia para la materia orgánica disuelta; 7) seguir desarrollando material de referencia no tóxico para los sistemas carbonatados, especialmente respecto del pH. Se necesitan materiales de referencia que respondan a la creciente demanda de ese tipo de soluciones para las investigaciones sobre la acidificación del océano.

Otros temas expuestos en la reunión fueron: 1) un estudio de comparación realizado en el Báltico, que evidenciaba un alto grado de comparabilidad de los datos recogidos en tres buques mediante operarios preparados que utilizaban botellas de muestreo y almacenamiento de un mismo diseño con idénticos procedimientos; 2) métodos desarrollados por el IFREMER que reducen los problemas de interferencia al medir muestras de diferente salinidad en un autoanalizador; 3) mediciones de oxígeno mediante sensores de optodo de respuesta rápida, y los resultados más recientes de un estudio de viabilidad de un material de referencia respecto del oxígeno disuelto.

Рабочее резюме

Совещание объединенной Исследовательской группы МОК-МСИМ по стандартам для питательных веществ (ИГСПВ) было проведено в Париже (Франция) 23–24 марта 2010 г. Обсуждение было сосредоточено на текущей деятельности ИГСПВ и планах в отношении расширения международного взаимодействия в целях обеспечения глобальной сопоставимости данных о питательных веществах, поступающих из различных океанов мира. На совещании присутствовало 32 ученых и экспертов из 11 стран и два делегата от МОК.

В настоящее время основная проблема сравнения данных о концентрации питательных веществ в океане заключается в том, что при сравнении данных, полученных на различных маршрутах, в точках пересечения такие данные оказываются недостаточно сопоставимыми по сравнению с тем, что ожидалось при рассмотрении соответствующих методов группами по планированию ВОСЕ в 1993 г. Вместо ожидаемой сопоставимости (1%) перекрестные сравнения могут различаться на несколько процентов.

Проведенные в 2003 г., 2006 г. и 2008 г. сравнительные исследования по ЭМПВМВ выявили наличие согласованности, близкой к той, которую ВОСЕ считал возможным для лучших лабораторий, тогда как исследование 2008 г. показало также наличие ряда систематических ошибок в некоторых результатах. Ценность этих исследований по взаимному сравнению заключалась в том, что они способствовали распространению информации о материалах. На начало 2011 г. запланировано еще одно исследование, охватывающее 70 лабораторий, работа которых связана с глубоководными участками моря.

Из этих усилий можно извлечь важные уроки в отношении того, какие метаданные должны сопровождать данные о питательных веществах при их внесении в банк данных. В ходе совещания обсуждалась необходимость внедрения эффективной практики представления метаданных наряду с использованием ЭМПВМВ. В связи с этим мы подготовим стандартную форму для сообщения метаданных для будущих экспедиций и исследований по взаимному сравнению данных.

Национальный метрологический институт Японии (НМИЯ) осуществляет сертификацию трех уровней эталонных материалов для питательных веществ в морской воде (ЭМПВМВ) в отношении нитратных, нитритных, фосфатных и силикатных питательных веществ в морской воде – чрезвычайно низкая концентрация, средняя концентрация и высокая концентрация. Образцы воды с низкой и высокой концентрацией уже собраны. Было решено собрать и представить в 2010 г. образцы морской воды для получения/сертификации ЭМПВМВ со средним уровнем концентрации на основе использования воды с глубоководных участков Атлантического океана.

Сообщалось о подготовке пересмотренного руководства по анализу питательных веществ, которую осуществляет ИГСПВ. Было решено завершить подготовку пересмотренного руководства, включая СОП, к 1 августа 2010 г. Оно будет опубликовано в онлайновом режиме Программой гидрографических исследований в Мировом океане на базе судов (ПГИМОС). Необходимо найти конкретного издателя этого руководства, такого как МОК или МСИМ.

Участники совещания решительно поддержали идею организации семинара на борту судна в 2013/2014 гг., в ходе которого основные группы могли бы провести полное взаимное сравнение всех процедур, включая аналитические методы, применяемые на борту исследовательского судна.

Были сообщены результаты, полученные на основе растворов ЭМПВМВ, использованных в ходе повторных измерений на маршруте P6 в 2009/2010 гг. Скриппским институтом океанографии (СИО). Отчет показал, что можно добиться значительных улучшений в плане внутренней сопоставимости данных и сопоставимости с данными предыдущего плавания по маршруту P6 в 2003 г., совершенного Японским агентством по морским наукам и технологии (ЯМСТЕК), в ходе которого также использовались ЭМПВМВ.

Данные по результатам теста на общую стабильность, проведенного десятью лабораториями, показаны в отношении нитратов, фосфатов и силикатов. За исключением данных ЯМСТЕС в представленных данных нет ожидавшейся последовательности. Причины этого необходимо изучить. Вместе с тем данные ЯМСТЕК, по всей видимости, указывают на то, что ЭМПВМВ являются стабильными за период, проанализированный до настоящего времени.

Сообщалось о создании эталонных материалов для растворенного органического вещества. Результаты теста по ЭМПВМВ для растворенного органического вещества показали, что ЭМПВМВ не эффективны для растворенного органического вещества. Запланирована дальнейшая работа.

Сообщалось о создании нетоксичных эталонных материалов для карбонатных систем. Это необходимо для удовлетворения растущего спроса на такие растворы для работы, связанной с закислением океана. Для оценки закисления океана необходим контроль качества pH морской воды, поэтому мы намерены разработать эталонные материалы для pH. Имеются следующие варианты эталонных материалов для pH морской воды: существующие токсичные ЭМ, которые уже сертифицированы для таких параметров, как количество растворенного неорганического углерода и общая щелочность, нетоксичные ЭМ и раствор трис-буфера.

Обсуждался также смежный вопрос о распространении использования ЭМПВМВ для работы на шельфовых участках моря в порядке продолжения дискуссий, состоявшихся на совещании Рабочей группы МСИМ по химии моря (МКВГ) в 2010 г. МКВГ МСИМ сочла, что использование подходящих растворов ЭМПВМВ может быть полезным для взаимного сравнения данных по шельфовому морю и будет ценным дополнением работы с существующей системой тестирования эффективности контроля качества информации по мониторингу морской среды в Европе (КАСИМЕМЕ). Участники Парижского совещания обсудили возможную необходимость в дальнейшем изучении взаимной сопоставимости данных для лабораторий, работающих главным образом в шельфовых морях. Это дополнит запланированное мероприятие на 2011 гг., которое будет сосредоточено на лабораториях, занимающихся в основном глубоководными участками моря.

На Парижском совещании объединенной Исследовательской группы МОК-МСИМ по стандартам для питательных веществ 2010 г. все участники признали необходимость обеспечения сопоставимости данных о питательных веществах в Мировом океане на основе Международной системы использования шкалы питательных веществ (МСШПВ) и развития более широкого международного взаимодействия для этой цели. В частности, участники совещания достигли

согласия относительно (1) проведения в начале 2011 г. дальнейших исследований по взаимному сравнению ЭВПВМВ, охватывающих 70 лабораторий, работа которых связана главным образом с глубоководными участками моря; (2) подготовки формы сводки для метаданных измерений питательных веществ по маршрутам судов и в рамках исследований по взаимному сравнению; (3) осуществления взаимодействия с НМИЯ и сбора/предоставления в 2010 г. образцов морской воды для получения/сертификации ЭМПВМВ средней концентрации на основе использования воды с глубоководных участков Атлантического океана; (4) дальнейшего проведения тестов общей стабильности ЭМПВМВ десятью основными лабораториями до октября 2011 г.; (5) завершения работы в отношении пересмотра руководства по анализу питательных веществ, включая СОП, к 1 августа 2010 г. (это руководство будет опубликовано в онлайновом режиме программой ПГИМОС); (6) дальнейшего создания эталонных материалов для растворенных органических веществ; (7) дальнейшей разработки нетоксичных ЭМ карбонатных систем, особенно нетоксичных ЭМ pH. Эталонные материалы необходимы для удовлетворения растущего спроса на такие растворы для работы по проблеме закисления океана.

Дополнительные выступления на совещании касались следующих вопросов: (1) проведенного в отношении Балтийского моря сравнительного исследования, показавшего высокий уровень сопоставимости данных, собранных на трех судах подготовленными работниками, которые использовали бутылки для образцов и хранения одинаковой конструкции и применяли одни и те же процедуры; (2) разработанных ИФРЕМЕР методов, уменьшающих проблему интерференции при измерении образцов различной солености на автоматическом анализаторе; (3) измерений содержания кислорода на основе использования быстро реагирующих оптодных сенсоров и последних результатов исследования по вопросу о целесообразности создания ЭМ для растворенного кислорода.

1 Introduction

The comparability and traceability of chemical data in the world's oceans are fundamental issues in marine science, and they are particularly important for studies of global change.

A fundamental problem has been the lack of absolute reference materials against which analyses could be compared. The degree of comparability between laboratories has had to be assessed through comparison exercises. The International Council for the Exploration of the Sea (ICES) has supported five nutrient inter-comparisons since 1965 (UNESCO, 1965, 1967; ICES, 1967, 1977; Kirkwood *et al*., 1991; Aminot and Kirkwood, 1995). Other efforts to test comparability among nutrient analyses in sea water have also been carried out for over the last 30 years. In 2000 and 2002, the National Oceanic and Atmospheric Administration (NOAA)/National Research Council Canada (NRC) carried-out inter-comparisons between laboratories in the United States and Canada. These tested a seawater reference material for nutrients known as MOOS-1, which was provided by the NRC (Willie and Clancy, 2000; Clancy and Willie, 2003). In Europe, in 1993 a scheme called "Quality Assurance of Information for Marine Environmental Monitoring in Europe" – QUASIMEME (Topping, 1997) was started and has since evolved into a self sustaining proficiency-testing scheme (PTS). It supports individual laboratories in validating and maintaining the quality of their procedures for a wide range of determinants. However, QUASIMEME samples which are only measured once every six months are not long-term reference materials nor do they support the traceability and linkage of measurements from day to day. Materials that available in sufficient quantity that they can provide both long term and day to day comparability are needed in order to improve the overall precision within a laboratory, and to assess differences between laboratories in order to achieve a higher level of comparability. Most of the efforts that have been made to provide reference materials have been on too small a scale to meet the needs of the global community in measuring nutrients in seawater.

To change this situation work was started in the Meteorological Research Institute (MRI), Japan. Testing of the materials began with fully international inter-laboratory comparison. These started in 2003 with a study that included 18 laboratories (Aoyama, 2006; Aoyama *et al*., 2007). The tests expanded to 55 and 56 different laboratories worldwide, in 2006 and 2008 respectively (Aoyama, *et al*., 2008; 2010). Between 2006 I/C study and 2008 I/C study, an "International Workshop on Chemical Reference Materials in Ocean science" was held in Tsukuba, Japan on 29 October – 1 November 2007 and focused on the measurement of nutrients and of ocean CO_2 parameters. Participants of the workshop agreed to continue the international collaborations with the aim of establishing global comparability and traceability of the nutrients data from the world oceans. An "International Nutrients Scale System (INSS)" in seawater was agreed as the appropriate way to achieve this goal.

In 2009, a second INSS international workshop was held to discuss progress since 2007 and future tasks. The INSS workshop, organized by Michio Aoyama, Andrew Dickson, David Hydes, Akihiko Murata, Jae Oh, Patrick Roose and Malcolm Woodward, was held at UNESCO, Paris, France on 10–12 February 2009. The workshop focused on the ongoing international collaboration to establish global comparability of the nutrient data from the world oceans. The objectives of the workshop were to i) provide an updated manual of nutrients analysis by the INSS group; ii) review the usage of nutrients and carbonate system data in oceanography and, hence, the neces-

sity of INSS; iii) report results from the "2008 RMNS inter-comparison experiments"; iv) update the plan of "short-term stability experiment-characterization of RMNS" in 2009/2011; v) develop non-toxic CRMs for the CO_2 System; and vi) expand the RMNS for DOC, DON and DOP references.

The workshop was attended by 37 participants from 11 different countries representing the global scientific community, UNESCO-IOC, and other international organizations. The workshop included invited and contributed talks, poster presentations, and plenary discussions. Scientific discussion focussed on the need for comparability of nutrients data in the world ocean. The participants agreed that by establishing the INSS, the comparability and traceability of nutrients data in seawater could be ensured. Thus, not only the study for nutrients in seawater itself will move forward, but the amount of accumulated anthropogenic CO_2 can be more accurately evaluated, and that all of these measurements are essential for the study for global warming. Participants also agreed to publish a new manual for nutrient analysis, including analytical methods with the greatest accuracy currently being achieved by the ocean community (UNESCO, 2009).

The workshop produced a series of action items (see Chapter 5 – Action Items in IOC-UNESCO workshop report 224, IOC, 2009) and submitted a proposal of "ICES-IOC study group on Nutrients Standards - SGONS" to the 25th IOC general assembly (IOC, 2009a) and ICES annual meeting. This proposal was presented at the 25th IOC general assembly and adopted in June 2009. This proposal was also presented at the 2009 ICES Annual Scientific Conference and adopted in September 2009. The specific terms of references of the joint IOC-ICES SGONS (IOC, 2009b) are shown below.

Specific Terms of References of the Joint IOC–ICES SGONS

i) Develop and establish reference materials for nutrients in seawater (RMNS) collaborating with producers of currently available RMNS. Primary determinands are nitrate, nitrite, phosphate and silicate

ii) Collaborate with and encourage the National Metrology Institute of Japan to complete certification of RMNS for nitrate, nitrite, phosphate and silicate

iii) Develop new sampling and measurement protocols using the RMNS

iv) Carry out an international collaboration exercise to verify the stability of the reference materials and test the proficiency of the new protocols

v) Complete a revised nutrients analysis manual

vi) Distribute 10 000 bottles of reference material for nutrients to laboratories measuring nutrients as part of the CLIVAR Repeat Hydrography Programme to construct a global nutrient dataset referenced to the new RMNS

vii) Promote the use of RMNS to aim for global acceptance in order to enable reliable comparability between global nutrient data sets, and to investigate the feasibility of expanding RMNS to include ammonium and dissolved organic matter

viii) Collaborate with the ocean science community that uses chemical reference materials, including carbonate system reference material for dissolved inorganic carbon, total alkalinity and pH, and dissolved oxygen in seawater

Thereafter the joint IOC-ICES SGONS started its activity according to the terms of references. The agreements at workshops in Tsukuba 2007 and Paris 2009 marked epochs in the history of nutrients comparability. The great step of the SGONS activity after two workshops was the 2010 Paris meeting of the joint IOC-ICES SGONS to advance international collaboration in establishing global comparability of nutrients data in the world oceans. In this report we describe discussions at the meeting and agreed action items.

2 Discussion-Session summary

2.1 Session 1: Chairperson David Hydes

The meeting was opened by Michio Aoyama, representing SGONS who welcomed the 32 international delegates to the first meeting of the IOC-ICES SGONS. Luis Valdes Head of Ocean Science Section of IOC, then followed with a welcome on behalf of IOC who were hosting the meeting. He pointed out the importance of groups like SGONS to IOC because among other things they contribute to improving the ability of marine scientists to make effective global assessments.

Michio Aoyama then reviewed the history behind the meeting, leading onto a consideration of the present state of progress and what future developments might be. The work of SGONS follows on from number of efforts over the last twenty years to improve comparability of nutrient measurements both other time in individual laboratories and between laboratories. Much of this work was done within the ICES community and Alain Aminot (IFREMER) played major role in this work (Aminot and Kerouel, 1991, 1995; Aminot and Kirkwood, 1995). This laid the basis of the work currently being done in Japan by Aoyama (MRI) and Ota (Kanso Technos). The basic problem is that when data are obtained on different cruises and the compared at cross over points, the comparability is not as good as would be hoped for a when methods were reviewed by the WOCE planning groups in 1993. Rather than the 1 % comparability expected, cross over comparisons may be several percent in variance.

Working with Ota and Kanso Technos a factory system capable producing large batches of reference solutions (RMNS) has been set up. This has provided materials used in inter-comparison studies (Aoyama, 2006; Aoyama *et al*., 2007, 2008 and 2010a). These studies have found agreement close to what WOCE considered possible for the better laboratories, while the 2008 exercise also showed indications of a number of systematic errors in some of the results. These inter-comparisons have been valuable in spreading awareness of the materials and a further exercise is to be planned for 2011 which will be expanded to 70 laboratories primarily working in the deep sea.

Using these solutions may produce an improved comparability but a second point is the need to obtain an overall measure of accuracy. For this reason, a subset of the solutions produced by Kanso, will be certified by the National Metrology Institute of Japan (NMIJ). This was discussed further throughout this current meeting. A critical point is that NMIJ can make accurate measurements but that the error bars on this certification may be wider than the comparability that should be achievable between labs when the RMNS solutions are used.

Asami Murao of Kanso Technos then provided an illustrated guide to the production of the RMNS by Kanso (Ota *et al*., 2010). A key point of this description was the new steps that have been put into place to improve the procedures at the plant. This was because the extensive testing of the solutions done by Kanso, showed that four

batches of RMNS were contaminated and consequently gave results that were more variable than earlier batches. An important request from the meeting was that Kanso should state what the target precision of their work is. At the moment they are aiming for the best possible value, but it was felt that this should be quantified. The numbers and types of solutions so far produced were then described and the numbering system explained. A report on the problems that have been encountered has been prepared and this will be distributed to all those attending the meeting.

Karel Bakker (NIOZ) then presented results of the testing he carried out on the silicate standards solutions submitted to him by participants from the RMNS 2008 intercomparison. These tests were set up in response to the high variance (up to ±10 %) reported in the silicate data (Aoyama *et al*., 2010). forty vials of silicate stock standards, were collected. When the standards were diluted appropriately the variance was about 2%, suggesting that methodological difference were the cause of the higher variance in the 2008 RMNS results. Further tests were carried out that demonstrated the need for careful matching of the matrix of the calibration standards and the samples solutions. A paper describing these results will be published in a book entitled "Comparability of nutrients in the world's ocean INSS international workshop 10–12 February 2009, Paris on June 2010" (Bakker *et al*., 2010).

Toste Tanhua (IFM-GEOMAR) described why accurate measurements of nutrients are needed in the calculations of the oceanic inventories anthropogenic CO_2. This has led extensive work assessing nutrient data for the CARINA database now hosted by CDIAC (http://cdiac.ornl.gov/oceans/CARINA/about_carina.html). Important lessons can be learnt from this effort in demonstrating what metadata needs to accompany nutrient data when it is lodged in a databank. The need for establishing good metadata reporting practice alongside the use of RMNS was discussed throughout the meeting and Toste Tanhua agreed to contribute a section on this to the new nutrients manual that is being written by the SGONS.

2.2 Session 2: Chairperson Michio Aoyama

Michio Aoyama reported on the present status of certification of RMNS for nitrate, nitrite, phosphate and silicate at the National Metrology Institute of Japan. NMIJ is going to certify three levels of RMNS, Nutrient Seawater-Extreme Low Concentration, Middle Concentration and High Concentration (Kato, 2007). The middle one would be produced using Atlantic deep seawater and the high one would be produced using Pacific deep water. There is a delay to certification of RMNS due to problems with obtaining some suitable water from the Atlantic Ocean.

There were discussions on the certification and several questions arose from the participants. Michio Aoyama, therefore, will ask Dr. Hioki at NMIJ to report how NMIJ will carry out the certification of nitrate, phosphate and silicate concentration including near zero concentrations.

We also discussed the two ways to certify RMNS as stated in ISO guide 35 namely based on a consensus from the community and on the agreed two or more primary methods. Michio Aoyama pointed that when we want to have SI traceability of the nutrient concentration, it should be based on primary standards and primary methods and this is the theoretically the correct way to keep comparability for a long time.

2.3 Session 3: Chairperson Malcolm Woodward

This session was a report on the progress to date of the revised 'Gordon' protocols for the determination of nutrients in seawater. It has been submitted for inclusion on the

GO_SHIP (Global Ocean ship-based hydrographic investigations program) website (www.go-ship.org) for the on-line inclusion as part of a large series of different protocols for a suite of at-sea determinations.

This nutrient submission is led by David Hydes with a series of contributing co-authors. The title of the document is: "Determination of nutrients in seawater with high precision and intercomparability using gas-segmented continuous flow analysis".

David Hydes explained that this was a 'live' document and was there on the web to be changed and altered in response to comments from the community. David Hydes stressed the importance of the members of this meeting to go and read through and to send him comments urgently.

The manual is meant as a guide to 'best-practice' in performing nutrient measurements at sea, and is an updating of Gordon *et al*. (1993). Most importantly the manual is accompanied by a set of nutrient standard operating procedures, for sample collection, calibration solutions, the assessment of blanks, checking linearity of calibrations solutions and also for using certified reference materials.

The actually web site where the manual is residing at the present time is not the GO-SHIP site at the moment, but can be found at http://cdiac3.ornl.gov/hydrography

In the left hand column there is the link to the 'continuous flow automated analysis of seawater nutrients' and then on this page at the bottom are the attachments for the manual and also the standard operating procedures (SOP's). These are in pdf and word format.

It was pointed out that scientists will all use their own 'best practice' in reality, but that this must be reported along with the results, and that the 'check list of sources of error' is one of the most important sections. We need SOP's of the linearity of the calibrations carried out by individual labs, working through the document David highlighted some sections that are still blank and required input from the community and the relevant 'experts' to fill these in, for example we require a procedure to define the linearity and also how to confirm that in practice.

Metadata was discussed and it was suggested that a form/checklist was included in the next inter-laboratory test exercise sent out from Japan to make this reporting more formalised. There was a suggestion for using the 'Fischer' test and to have the excel spreadsheets sent out, this needed a volunteer from the community to be organised and co-ordinated by.

David Hydes went through the manual and highlighted the areas that required input from the community specifically, but he then requested that this review was carried out by all in as short a time as possible. GO_SHIP wish the manuals to be completed ready for the inclusion on the official website and the end of April was given as a deadline for additions, new writing and comments on the current draft version of the manual. This INSS community is the ideal group for making worthwhile contributions to this manual.

2.4 Session 4: Chairperson Karel Bakker

Three talks P-3 to P-5 were given in this session by the following speakers:

- P-3 Susan Becker, Michio Aoyama, Dan Schuller and Kenichiro Sato: Initial results from the use of RMNS during the CLIVAR P6 revisit cruise by SIO.

- P-4 Günter Nausch, B. Deutsch, T. Petenati, J. Voss, M.v.Weber: Harmonization and quality assurance in marine monitoring – how does sampling influence the comparability of data?
- P-5 Stephen Coverly, Roger Kérouel and Alain Aminot: Identifying, quantifying and correcting matrix effects in segmented-flow seawater analysis.

After each talk there was some time for questions and discussion.

First talk by Susan Becker, showing initial results for measurements of deep water and RMNS of the cruise CLIVAR P6 from Australia to Chile in 2009, divided in three legs. At the start a sample of the cruise deep water was preserved with $HgCl_2$ and measured simultaneously with RMNS and the CTD samples in every run.

Because four different RMNS with different nutrient levels were used, it was possible to calculate a "real" uncertainty value for those levels.

In the discussion afterwards Susan said that for every CTD station a new run was started with new calibration by means of diluting nutrient stock standards in LNSW.

If a particular nutrient NO_3, PO_4 or Silicate was plotted against time or CTD Station-number there was clearly a trend to be observed in the deep water data parallel to the result of the RMNS, with maximum variance of ±1 %. Michio Aoyama showed a plot made of a similar cruise for the Pacific carried out by JAMSTEC on the RV Mirai (Aoyama *et al*., 2005, 2007, 2009 and 2010b), resulting in a more coherent narrow banded graph for the data of RMNS used, in this case all runs were calibrated using the RMNS as standard to calibrate the equipment.

From both observations we can conclude that some variance within the cruise seems to come from the calibration in the P6 cruise, because results for the RMNS and deep water samples showing the same trend and variance from station to station.

Adjusting the data, by means of implementing a multiplying factor for each run based on the average of the deep water sample or the RMNS, would be expected to improve the data quality and make the data comparable with former P6 cruise and future cruises. The procedure developed from this experience of adjusting data with RMNS should the basis of a shipboard SOP in near future.

Second talk by Günter Nausch, showing results of an inter-comparison of sampling by three groups of people using the same procedure on three different ships in the Baltic Sea.

This inter-comparison study in sampling technique was done by three groups of people all trained in handling samples, using the same kind of bottles for nutrient sampling.

The ships as working platforms were as close as possible in the working area up to 80 meter as minimum distance still safe for navigation. Sampling was done with three CTD-Rosette systems; Niskin bottles for nutrients were closed at two depth intervals showing well mixed waters. After analyzing the bottles in one lab it was clear that for most parameters the samples from the different ships show statistical identical values for PO_4 and NO_3 within the reproducibility of the equipment and methods used, however silicate gave greater variance than this. This talk demonstrated that it is possible to go out at sea with three different groups to do your sampling for nutrients, as long they are well trained in doing so.

Third talk by Stephen Coverly, Identifying, quantifying and correcting matrix effects in segmented-flow seawater analysis:

In this talk Stephen Coverly gave a clear vision on how matrix effects are induced due to the effect of physical differences like salinity e.g. from the sample- to the wash-solution whilst passing the flow cell in an Auto Analyzer. Even if the segmented stream with bubbles pass the flow cell an effect will be observed depending on the amount of sample dilution in the system itself. By means of using special adapted software it is possible to minimize this matrix effect in the measurements, showing more smoothly formed peaks with almost no irregularity at the start or end of the peaks. This system can greatly improve the measurements for where samples with different salinities may need to be included in the same run such when working in estuaries or the Baltic Sea.

From a general discussion after the talks it seems that most people use PP or HDPE bottles (pre washed with diluted HCl and DIW) for sampling and reuse them continuously. If this is done you have to fill them regularly diluted HCl to act against bio-film growth. Much better is to use a new disposable bottle for each sample.

One other possibility could be using a 60 ml HDPE syringe with a three way valve connected; you can easy tap by means of tubing connected to the NISKIN bottles without any risk of contamination especially Ammonium, and no risk of rainwater dropping in the bottle. This last sampling technique should be tested for evaluation; advantage for filtrating your samples, it is easy to put an Acrodisc 0.2 um filter on the syringe in the lab.

2.5 Session 5: Chairperson Toste Tanhua

First report: Malcolm Woodward reported on the ongoing stability test:

- A number of laboratories are participating in this exercise, and a number of different batches of RMNS are being regularly measured.
- The measurements have been carried out since 2005 with one measurement round every 6 months, and the measurements are planned to continue to the end of 2011.
- The JAMSTEC lab has carried out the measurements more frequently.

Figures of the results of the measurements so far were shown for the 3 main analytes. There is large inter-laboratory variations with some clear outliers present in the data set. In fact, with the exception of the JAMSTEC data, the data presented are not particularly consistent. The JAMSTEC data however seems to suggest that the RMNS are stable for the time period analyzed so far.

Questions on the protocol for carrying out the measurements and the calibration were raised. It is important that the calibration is conducted vs. a primary standard, and not vs. a RMNS. It is apparent the results from most labs will have to be looked at in more detail in order to verify the stability of the RMNS, or to detect any drift in the data.

The second talk in this session was also by Malcolm Woodward, reporting on an inter-comparison exercise that was carried out by the UK and USA GEOTRACES community. For this study, 4 labs participated; samples were measured on board the ship by the Old Dominion University group in the USA and 4 sets of samples were frozen for later analysis by the participating laboratories. One of these sets were measured on-board the ship as the ship docked after the cruise, the others send of the other labs; all samples were measured within a few months.

The result was very discouraging, questioning the practice of freezing samples for later analysis on land. Of the analytes; the nitrate data faired the best, with spread in the order of 10 % between the labs. Next was phosphate data with a spread of about 25 % between the labs. Silicate data showed the largest spread, which decreased after the labs left the samples in the dark for 24 hours at room-temperature prior to measurements.

A short discussion followed on the necessary time needed for silicate samples to thaw; it seems that longer time is better (to a certain extent at least). It was suggested that freezing samples colder than -20 °C enhances this problem, but it was suggested that this could be solved with increasing the thawing time for the samples.

The third talk in this session was by Michio Aoyama, discussing the need for another inter-comparison action. It was agreed that:

1) next I/C should be carried out in early 2011;

2) the I/C should focus on "blue water"/deep hydrography, i.e. ocean salinity and "high" nutrient concentration;

3) around 70 sets of 6 bottles should be prepared for the exercise, but that more could be needed.

Michio Aoyama concluded that the I/C studies is a lot of work, but that he is willing to organize the more practical aspects of the coming I/C, i.e. inviting labs and sending out bottles etc. However, a committee was formed that should be responsible for evaluating the results and to contribute to the report. The members of the committee are:

- Karel Bakker – silicate
- Michio Aoyama – phosphate and nitrate/nitrite
- Malcolm Woodward – ammonium
- Takeshi Yoshimura – DOP, DON, DOC

It was agreed that Toste Tanhua should make a draft of a metadata protocol for nutrient measurements that will allow the committee to evaluate the data of the next IC study in greater detail. This metadata form could then be used also for reporting nutrient data from oceanographic research cruises (see Annex 3).

2.6 Session 6: Chairperson Anne Daniel

Michio Aoyama asked for a financial support to the Japanese government to prepare 10 000 bottles of RMNS which will be distributed to scientists who take part in CLIVAR Programme: the answer to this possible financing will be known at the end of May. A questionnaire will be sent to participants in June to know their RMNS needs (number per cruise, concentration ranges, etc).

The preparation of these 10 000 bottles of RMNS requires a collection of source seawater during the following 2010 cruises:

- Pacific surface water by Mirai/JAMSTEC and Ryofu/JMA
- Pacific deep water (August 2010), R/V Mirai
- Atlantic Ocean (June 2010), Thalassa by Pascal Morin
- Atlantic Ocean (July 2010), RRS Discovery by David Hydes
- Atlantic Ocean (October 2010), RRS Discovery by Malcolm Woodward
- Tropical Atlantic (October 2010), R/V Meteor by Toste Tanhua

- Mediterranean sea, Olivier Grosso
- Mediterranean Deep water, Pascal Morin
- Southern Ocean (December 2010)

For information, to produce 1500 bottles of RMNS (2000 bottles but 500 are used by Kanso for tests), 250 L of source seawater is needed. In order to resolve the bacterial problems observed during a previous collection of seawater in Atlantic, an on-line UV system need to be used to sterilize the seawater on board. Michio Aoyama will send a detailed protocol describing the sampling procedure.

In the following discussion the meeting strongly endorsed the idea of a ship board workshop in 2013/2014 during which major groups would carry out a full inter-comparison of all procedures including analytical methods on board a research ship.

2.7 Session 7: Chairperson Akihiko Murata

In this session, first, Malcolm Woodard briefly talked about possibility of having reference material for ammonium. Currently there are many issues to be resolved for the success of reference material for ammonium. Takeshi Yoshimura reported developing reference materials for dissolved organic matter. He tested RMNS for dissolved organic matter. The results showed that RMNS was not good for dissolved organic matter. He also introduced development of RM based on his own method. The development is still underway.

2.8 Session 8: Chairperson Michio Aoyama

Collaboration with the ocean science community that uses chemical reference materials, including carbonate system reference material for dissolved inorganic carbon, total alkalinity and pH, and dissolved oxygen in seawater was discussed.

Akihiko Murata reported on the development of a non-toxic RM for the carbonate systems. These are needed to support the growth in demand for such solutions for work on ocean acidification. He talked about the development of RMs for oceanic CO_2 measurements. He reported on quality control of seawater pH, which is indispensible for the evaluation of ocean acidification, and the intention to develop reference material for pH. He suggested three candidates for RM for seawater pH are as follows: (1) Existing toxic RM, which is already certified for DIC and TA. (2) Non-toxic RM and (3) Tris buffer.

Hiroshi Uchida reported on the development of RM for dissolved oxygen. He talked about high-quality oxygen measurements by using fast-responding optode sensors in which he showed present state of oxygen sensors, issues in oxygen measurements. He also pointed out on lack of comparability of dissolved oxygen measurements and errors in the Winkler's method. Then he showed latest results of feasibility study of RM of dissolved oxygen.

2.9 Session 9: Chairperson Akihiko Murata

Michio Aoyama reported a global nutrient data synthesis effort, which is now being conducted by his laboratory. The main purposes of doing this are to improve comparability of nutrient data, and to investigate temporal and spatial changes of nutrients based on quality-controlled data. He has used historical data such as WOA05 together with recently measured nutrient data based on RMNS. He has compared nutrients data not based on RMNS with those based on RMNS at crossover points. Then he decided biases of nutrients data not based on RMNS. He reported that more reli-

able distributions of nutrients, stoichiometric ratio (Redfield ratio), temporal changes, etc. could be obtained by using data, biases of which are corrected. There were questions about levels of historical data and how to get rid of biases.

2.10 Sessions 10 and 11: Chairperson David Hydes

To date the focus of activity for the development of the RMNS materials has been the deep sea and the need to improve on the comparability of hydrographic measurements of nutrients beyond what was actually achieved during in the main during WOCE and subsequent CLIVAR cruises. However the original groups working on the nutrient inter-calibration exercises lead by Alain Aminot were mostly ICES related laboratories whose concern was improving the comparability of nutrient measurements in shelf sea waters. Another related outcome of that work was QUASIMEME (www.quasimeme.org). The acronym QUASIMEME comes from its EU project name "Quality Assurance of Information for Marine Environmental Monitoring in Europe" which was founded in 1993. QUASIMEME provides a very valuable role is assessing the performance of laboratories but the two lots of nutrient samples it distributes per year are not sufficient to provide day to day control of data output. The work of SGONS was presented at the 2010 meeting of the ICES Marine Chemistry working group as part of the process of linking the work of SGONS to that of other ICES and IOC evidence groups. The discussion that meeting considered was that RMNS materials from shelf sea waters would be of considerable use to the community, and that it should be used in conjunction with participation in QUASIMEME. The recommendation of the MCWG was that it should be discussed with SGONS that a winter surface water collected adjacent to the NW European Shelf and a winter Baltic Sea surface water (salinity >10) be added to the list of RMNS materials.

The Paris meeting then discussed the possible need for a further global inter-comparison exercise for laboratories working mainly in shelf seas. This would complement the planned 2011 exercise, which would focus on laboratories whose main concern was deep ocean waters.

3 Conclusions

A meeting of the joint IOC-ICES Study Group on Nutrient Standards (SGONS) was held in Paris, France, on 23–24 March 2010. It focused on the ongoing activity of SGONS and plans for extended international collaborations to establish global comparability of the nutrient data from the world's ocean. Thirty two scientists and experts from 11 countries and 2 delegates from IOC attended the meeting.

The basic problem on comparability of nutrients data in the world ocean is that when data is obtained on different cruises are compared at cross over points, the comparability is not as good as was hoped for a when methods were review by the WOCE planning groups in 1993. Rather than the 1 % comparability expected, cross over comparisons may be several percent out.

Recent RMNS I/C studies in 2003, 2006 and 2008 have found agreement close to what WOCE considered possible for the better laboratories, while the 2008 exercise also showed indications of a number of systematic errors in some of the results. These inter-comparisons have been very valuable in spreading awareness of the materials and a further exercise is to be planned for 2011 which will be expanded to 70 laboratories primarily working in the deep sea.

Important lessons can be learnt from this effort in demonstrating what metadata needs to accompany nutrient data when it is lodged in a databank. The need for establishing good metadata reporting practice alongside the use of RMNS was discussed throughout the meeting. Therefore we will prepare a form for metadata report for cruises and I/C studies.

National Metrology Institute of Japan, NMIJ is certifying three levels of RMNS for nitrate, nitrite, phosphate and silicate Nutrient Seawater-Extreme Low Concentration, Middle Concentration and High Concentration. There is a delay to certification of RMNS due to problems with obtaining any suitable water from the Atlantic Ocean. We therefore will continue the collaboration with NMIJ and collect/provide seawater in 2010 to produce/certify middle level of certified RMNS using Atlantic deep water.

The preparation of the revised nutrients analysis manual which is being undertaken by the SGONS was reported. It was agree to complete the revised manual including SOPs by 1 August 2010. It will be published on line by Go-Ship. A definitive publisher of the manual such as IOC or ICES needs to be found.

Results obtained with RMNS solutions used on the P6 reoccupation cruise in 2009/2010 by SIO was reported. In the report, it is shown that considerable improvement could be made in the internal comparability of the data by referencing it to the RMNS results and related good comparability with the previous P6 cruise in 2003 by JAMSTEC when RMNS were also used. The meeting strongly endorsed the idea of a ship board workshop in 2013/2014 during which major groups would carry out a full inter-comparison of all procedures including analytical methods on board a research ship.

This inter-comparison study in sampling technique was done by three groups of people all trained in handling samples, using the same kind of bottles for nutrient sampling. As a result, clearly demonstrated here, it is possible to go out at sea with three different groups to do your sampling for nutrients, as long they are well trained in doing so.

A developed segmented flow analytical system reported by Stephen Coverly *et al*. can greatly improve the measurements for estuarine work for instance, samples with several salinities in the field from coast to sea, or in seas with different salinities in one CTD like the Baltic or in Fjords with several layers of saline/ fresh water above each other.

Figures of the results of the global stability test by ten core laboratories were shown for nitrate, phosphate and silicate. There is large inter-laboratory variations with some clear outliers present in the data set. In fact, with the exception of the JAMATEC data, the data presented are not particularly consistent. The JAMSTEC data however seems to suggest that the RMNS are stable for the time period analyzed so far.

On another Inter-comparison action, it was agreed that:

1) next I/C should be carried out in early 2011;

2) the I/C should focus on “blue water”/deep hydrography, i.e. ocean salinity and “high” nutrient concentration;

3) around 70 sets of 6 bottles should be prepared for the exercise, but that more could be needed.

The preparation of 10 000 bottles of RMNS requires a collection of source seawater during the following 2010 cruises:

- Pacific Ocean by Mirai/JAMSTEC and Ryofu/JMA
- Pacific deep water (August 2010), R/V Mirai
- Atlantic Ocean (June 2010), Thalassa by Pascal Morin
- Atlantic Ocean (July 2010), RRS Discovery by David Hydes
- Atlantic Ocean (October 2010), RRS Discovery by Malcolm Woodward
- Tropical Atlantic (October 2010), R/V Meteor by Toste Tanhua
- Mediterranean sea, Olivier Grosso
- Mediterranean Deep water, Pascal Morin
- Southern Ocean (December 2010)

Developing reference materials for dissolved organic matter was reported. The results of a test on RMNS for dissolved organic matter showed that RMNS was not good for dissolved organic matter. The development is still underway.

The development of non-toxic RM of the carbonate systems was reported. These are needed to support the growth in demand for such solutions for work on ocean acidification. Quality control of seawater pH is indispensible for the evaluation of ocean acidification, therefore we intend to develop reference material for pH. There are three suggested candidates for RM for seawater pH - Existing toxic RM (which is already certified for DIC and TA), non-toxic RM and Tris buffer.

High-quality oxygen measurements by using fast-responding optode sensors were reported. It is pointed out that a lack of comparability of dissolved oxygen measurements and errors in the Winkler's method. The latest results of feasibility study of RM of dissolved oxygen were presented.

The related point of the extension of the use of RMNS for work in shelf sea water was also discussed, this followed on from discussions at the ICES Marine Chemistry Working Group meeting on 2010. The ICES MCWG considered that the use of suitable RMNS solutions would be valuable for improving the inter comparability of shelf sea data and be a valuable complement to work with the existing QUASIMEME proficiency testing scheme. The Paris meeting then discussed the possible need for a further global inter-comparison exercise for laboratories working mainly in shelf seas. This would complement the planned 2011 exercise, which would focus on laboratories whose main concern was deep ocean waters.

At the 2010 Paris meeting of the joint IOC-ICES SGONS, all participants recognized the need to establish comparability of nutrients data in the world ocean through International Nutrients Scale System (INSS), and build more international collaborations for this goal. In particular, the meeting participants decided to: (1) set up a further I/C studies of RMNS for early 2011 which will be expanded to 70 laboratories primarily working in the deep sea; (2) prepare a form for metadata report of nutrients measurements for cruises and I/C studies; (3) keep collaboration with NMIJ and to provide seawater in 2010 to produce and then certify a middle level of certified RMNS using Atlantic deep water; (4) continue the global stability test of RMNS by ten core laboratories until October 2011, (5) complete the revised nutrients analysis manual including SOPs by 1 August 2010, (it will be published on line by Go-Ship); (6) continue development of reference materials for dissolved organic matter; (7) continue development of non-toxic RM of the carbonate systems especially an RM of pH. These are needed to support the growth in demand for such solutions for work on ocean acidification.

4 Action items and related ToRs of SGONS

1) A further I/C study of RMNS will be planned for early 2011 which will be expanded to 70 laboratories primarily working in the deep sea. ToR (iv).

2) A form will be set up for metadata reporting of nutrients measurements for cruises and I/C studies. ToR (iii) and (v).

3) Collaboration with NMIJ will be continued and it was agreed to provide seawater in 2010 to produce/certify middle level of certified RMNS using Atlantic deep water. ToR (ii).

4) The global stability test of RMNS by ten core laboratories will be continued until October 2011. ToR (iv).

5) The revised nutrients analysis manual including SOPs will be completed by 1 August 2010. It will be published on line by Go-Ship. A definitive publisher of the manual such as IOC or ICES needs to be found. ToR (v).

6) A ship board workshop will be organised for 2013/2014 during which major groups around the world would carry out a full inter-comparison of all procedures including analytical methods on board a research ship. Funding for this proposal needs to be found though.

7) Development of reference materials for dissolved organic matter will be continued. ToR (vii).

8) Development of non-toxic RM of the carbonate systems will be continued. These are needed to support the growth in demand for such solutions for work on ocean acidification. Quality control of seawater pH is indispensible for the evaluation of ocean acidification, therefore we intend to develop reference material for pH. ToR (viii)

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Annex 1: Agenda

23 March (Tue) 2010

09:15～09:45	WORKSHOP REGISTRATION
09:45～10:00	OPENING SESSION Chairperson: David Hydes
10:00～11:00	SESSION 1 Chairperson: David Hydes
	Develop and establish reference materials for nutrients in seawater (RMNS) collaborating with producers of currently available RMNS. Primary determinands are nitrate, nitrite, phosphate and silicate. Aoyama Report: on progress with the production of RMNS materials. Including list of what RMNS materials are available and the ocean areas they are suitable for use in.
11:00～11:30	COFFEE
11:30～12:10	SESSION 1 Continued
P-1	Karel Bakker : The inconvenient truth of Silicate analysis
P-2	Toste Tanhua : On the importance of accurate nutrient data on oceanic anthropogenic carbon calculations.
12:10～12:50	SESSION 2 Chairperson: Michio Aoyama
	Collaborate and encourage National Metrology Institute of Japan to complete certification of RMNS for nitrate, nitrite, phosphate and silicate. Aoyama Report: for Dr. Hioki, NMIJ on the certification.
12:50～14:30	LUNCH
14:30～15:10	SESSION 3 Chairperson: Malcolm Woodward
	Complete and publish a revised nutrients analysis manual. David Report: on progress with the revised nutrients manual.
15:10～15:50	SESSION 4 Chairperson: Karel Bakker

	Develop new sampling and measurement protocols using the RMNS (which will form part of the manual).
P-3	Susan Becker, Michio Aoyama, Dan Schuller and Kenichiro Sato : Initial results from the use of RMNS during the CLIVAR P6 revisit cruise by SIO.

15:50～16:20	COFFEE

16:20～17:20	SESSION 4 Continued
P-4	G. Nausch, B. Deutsch, T. Petenati, J. Voss, M.v.Weber: Harmonization and quality assurance in marine monitoring – how does sampling influence the comparability of data?
P-5	Stephen Coverly, Roger Kérouel and Alain Aminot : Identifying, quantifying and correcting matrix effects in segmented-flow seawater analysis.
	Discussion

18:00～20:00	Reception (Coffee Bar of the Moillis Building, UNESCO)

24 March (Wed) 2010

09:00～10:00	SESSION 5 Chairperson: Toste Tanhua
	Carry out an international collaboration exercise to verify the stability of the reference materials and test the proficiency of the new protocols.
	Report: on a progress with ongoing stability test in 2009.
P-8	Malcolm Woodward: A protocol for stability tests–inter-laboratory comparison study in 2010.

10:00～10:40	SESSION 6 Chairperson: Anne Daniel
	Distribute 10000 bottles of RMNS to laboratories measuring nutrients as part of the CLIVAR Repeat Hydrography Program to construct a global nutrient dataset referenced to the new RMNS.
	Report : on progress with planning this action and the need for water of appropriate composition

10:40～11:10	COFFEE

11:10～11:50	SESSION 7 Chairperson: Akihiko Murata
	Investigate the feasibility of expanding RMNS to include ammonium and dissolved organic matter.
	Report : on progress

P-6	Takeshi Yoshimura : Developing reference materials for dissolved organic matter analysis, targeting completion in 2013
11:50～12:30	SESSION 8 Chairperson: Michio Aoyama
	Collaborate with the ocean science community that uses chemical reference materials, including carbonate system reference material for dissolved inorganic carbon, total alkalinity and pH, and dissolved oxygen in seawater. Murata Report : on progress
P-7	Hiroshi Uchida : High-quality oxygen measurements by using fast-responding optode sensors
12:30～14:00	LUNCH
14:00～14:40	SESSION 9 Chairperson: Akihiko Murata
	Promote the use of RMNS to aim for global acceptance in order to enable reliable comparability between global nutrient data sets
P-9	Michio Aoyama : Global nutrients data synthesis based on the cruises with Reference Material of Nutrients in Seawater.
14:40～15:20	SESSION 10 & 11 Chairperson: David Hydes
	Report to SSGHIE on your plans to promote cooperation between EGs covering similar scientific issues. Report: on discussion of RMNS development within the ICES Marine Chemistry Working Group. Report to SSGHIE on potential and current contributions of your EG to the Strategic Initiative on Coastal and Marine Spatial Planning (SICMSP).
15:20～15:40	CLOSING SESSION Chairperson: Michio Aoyama

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Annex 3: Metadata for Reporting on Nutrient Measurements

Metadata for reporting on nutrient measurements Ver. 2.0

Reply by E-mail | Print this form

General Information:

Data Serial _____ Vessel name _____ Cruise ID (EXPOCODE) _____ Leg _____

Country _____ Vessel ID _____ Experiment Name _____ CTD stations Number _____

Date and Port of departure _____ Geographical coverage (e.g. North Atlantic; 30°N to 50°N and 60°W to 10°W) _____

Date and Port of arrival _____

Significant part of the information required below is specific for the nutrient measurements. Several of these fields will be generic for a particular lab, i.e. will only have to filled out once by each lab; variations to the standard procedures can easily be edited in.

Nutrients Measurements:

1. Investigator

Name _____ Phone _____ Email _____

Organization _____

Address _____

2. Variables description

Variable names _____

Reporting Units _____

3. Date of measurement date of reception or collection of samples _____

Method Description:

1. Instrument: State instrumentation used for the measurements. For instance: Braan-Luebbe TrAAcs 800 autoanalyzer. _____

3. State settings such as the sampling/rinsing cycles, temperatures, air/nitrogen in the gas bubbles etc. _____

4. Dilution of high concentration samples _____

5. Environmental information such as lab temperature (e.g. 20-24°C variable). _____

6. Sampling containers (e.g. 100 ml polypropylene bottles, reused). _____

7. Did you filtrate your samples; if so, state details. _____

8. Storage (e.g. dark at 8°C). This includes information on samples stored for a longer time and analyzed on-shore after the cruise. T° and time of storage, standard or document reference if applicable, respect of continuous refrigeration yes/no _____

9. Poisoning of samples? _____

10. Thawing procedures if sample was frozen. _____

2. State method for each measured parameter, and appropriate reference. For instance: Ammonia was measured with o-phthalaldehyde (OPA) in the presence of borate buffer solution and sodium sulfite; fluorescence measured at 460 nm, excitation at 370 nm. Method no G-327-05 Rev 3 (Seal Analytics), Kerouel and Aminot, 1997. State any deviations in your set-up from the reference method or any modification from the standard instrument. _____

Reagents:

1. Brands and stock information of the reagents/salts used. _____

2. Where the solutions prepared on the ship, or pre-made in the lab prior to cruise. _____

3. Which medium was used for the reagents (e.g. MilliQ, destwater). _____

Standardization:

1. How were your stock solutions prepared (initial salts, medium), + method (volumetric; mass) _____

2. How were the stock solutions diluted to working concentrations (medium), + method (volumetric; mass) _____

3. Blank measurements (medium) (or balance (calibration, precision,...)) _____

4. Which pipettes were used? State calibration information of the pipettes. _____

Reference Material:

1. Did you use any certified reference material or certified standards (state batch numbers, producer etc.). _____

2. Did you correct raw data before you submit your data? _____

Quantification procedures:

1. Mathematical formula used for the calculation of concentration _____

2. Matrix corrections (method used to quantify corrections) _____

3. Calibration curves/ranges (number of points used for calibration curve, concentration used for calibrants) _____

3. Did you do carry over correction? _____

4. Did you do base line drift correction? _____

5. Blank corrections (Null and refractive index blank) _____

6. Recalculation of run? (state modifications) _____

Data Quality:

1. Provide your best estimate of precision and accuracy.(? Cf mail) _____

2. State how these numbers were obtained (e.g. by measurements of X duplicates and by running X number of Certified Reference Material). _____

3. Number of samples/doubles measured _____

4. Detection limit and quantification limit (method used, formula for calculation or parameters used) _____

5. State uncertainty components; uncertainty calculation, confidence interval (or coverage factor) _____

6. Method used to round off results to the number of significant digits _____

Annex 4: List of acronyms

CARINA	Carbon Dioxide in the Atlantic Ocean
CDIAC	Carbon Dioxide Information Analysis Center
CLIVAR	Climate Variability and Predictability
CRMs	Certified Reference Materials
CTD	Conductivity, Temperature and Depth sensor
DIC	Dissolved Inorganic Carbon
DIW	Distilled Water
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphate
EG	Expert Groups
GEOTRACES	An International Study of the Marine Biogeochemical Cycles of Trace Elements and Their Isotopes
GO_SHIP	Global Ocean ship-based hydrographic investigations program
HDPE	High Density Poly Ethylene
I/C	Inter-comparison
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
INSS	International Nutrients Scale System
IOC	Intergovernmental Oceanographic Commission
IOS	Institute of Ocean Sciences, Canada
ISO	International Organization for Standardization
JAMSTEC	Japan Agency for Marine-Earth Science and Technology
JMA	Japan Meteorological Agency
LNSW	Low Nutrient Sea Water
MCWG	Marine Chemistry Working Group
NIOZ	Royal Netherlands Institute for Sea Research
NMIJ	National Metrology Institute of Japan
NRC	National Research Council Canada
PP	Poly Propylene
PTS	Proficiency-Testing Scheme
QUASIMEME	Quality Assurance of Information for Marine Environmental Monitoring in Europe
R/V	Research Vessel
RM	Reference Material
RMNS	Reference Materials for Nutrients in Seawater
RRS	Royal Research Ship
SGONS	The Joint ICES-IOC Study Group on Nutrients Standards
SICMSP	Strategic Initiative on Coastal and Marine Spatial Planning
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedures
SSGHIE	SCICOM (Science Committee) Steering Group on Human Interactions on Ecosystem
TA	Total Alkalinity

ToR	Terms of Reference
UNESCO	United Nations Educational Science and Culture Organization
UV	Ultra Violet
WOA	World Ocean Atlas
WOCE	World Ocean Circulation Experiment