Intergovernmental Oceanographic Commission

Workshop Report No. 224

2009 International Nutrients Scale System (INSS) Workshop Report

UNESCO, Paris, France
10-12 February, 2009

IOCCP Report Number 16

UNESCO 2009


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Abstract:

An International Nutrients Scale System (INSS) workshop was held at UNESCO, Paris, France on 10-12 February 2009. The workshop focused on the ongoing international collaboration of establishing global comparability of the nutrient data from the world's ocean. 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 necessity 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.

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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. An "International Workshop on Chemical Reference Materials in Ocean science" was held in Tsukuba, Japan on 29 Oct. – 1 Nov. 2007 and focused on the measurement of nutrients and of ocean CO_2 parameters. In the meeting, we discussed the current status of available chemical reference materials in ocean science, and agreed to establish international collaborations in order to promote the use of reference materials, and to develop new chemical reference materials where they were not available to researchers. 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 International Nutrients Scale System (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 of establishing 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 necessity 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 eleven different countries representing the global scientific community, UNESCO-IOC, and other international organizations. The workshop was comprised of 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. The results will contribute to the study of nutrients in seawater, as well as the study of both global warming and ocean acidification, due to increased emissions of anthropogenic CO_2.

The workshop produced a series of action items (see Chapter 5-Action Items) and submitted a proposal of "ICES-IOC study group on Nutrients Standards - SGONS" to the 25th IOC general assembly and ICES annual meeting. This proposal was presented at the 25th IOC general assembly was adopted in June 2009.

1.1 BACKGROUND OF THE 2009 INSS INTERNATIONAL WORKSHOP

It is a fundamental requirement when investigating major issues like global change to be absolutely confident in the data sets that are being compared. For nutrients data sets, these must be seen to be comparable and traceable when interpreting results from separate laboratories in many different countries. This will then lead to confidence in any of these global changes that are reported by the community. However, as Climate Change 2007 – The Physical Science Basis (IPCC2007) report stated, adequate comparability and traceability have not yet been achieved. The IPCC2007 report comments as follows on nutrients comparability:

"Using the same data set extended to the world, large regional changes in nutrients ratios were observed (Li and Peng, 2002) but no consistent basin-scale patterns. Uncertainties in deep ocean nutrients observations may be responsible for the lack of coherence in the nutrients 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)".

In 1990s, Ridout (1999) pointed out that in 1993 the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials (GESREM, 1993) drew attention to an urgent need for the development of certified reference seawater for dissolved nutrients. Dickson (2001) also pointed out the need to develop certified reference seawater which can cover several determinands all in one bottle.

During the WOCE science programme, WHPPC recognized the importance of comparability of WOCE nutrients data world wide. They recommended to all WOCE cruise PIs to participate in the ICES 6th inter-comparison, however, it could not done because the ICES 6th inter-comparison was cancelled.

In the 1990s a number of studies were organized under the ICES umbrella. These studies were well documented (see Aminot et al., 1995 and Aoyama, 2006 in details). In Europe, this led into the setting up of QUASIMEME (Topping, 1997). QUASIMEME is useful from the point of validating the procedures of individual laboratories for a wide range of determinands. However, this system is inadequate for supporting the traceability that is required to link measurements from one day to another in order to improve the overall precision within a laboratory, or to achieve a known level of comparability between different laboratories.

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

In 2003 Michio Aoyama, of the Meteorological Research Institute (MRI), Japan, organized an inter-laboratory comparison study which include 18 laboratories (Aoyama, 2006, Aoyama et. al, 2007). In 2006 Michio Aoyama, working with Hidekazu Ota, of the General Environmental Technos Co., Ltd. (KANSO), Japan,

organized a second inter-comparison study which included 55 different laboratories world wide (Aoyama, et al., 2008). Both inter-laboratory comparison studies clearly show that the global use of reference materials for nutrients in seawater would greatly improve the comparability of nutrients data in the world's oceans.

In early 2007 Michio Aoyama visited NOC in Southampton, UK, to discuss the results of the inter-calibration exercise. This was extended to an invitation to the European participants in the inter-calibration and other interested nutrients chemists, all to attend a discussions meeting at NOC.

Following on from this an International Workshop on Chemical Reference Materials in Ocean Science was held in Tsukuba, Japan, on 29 October to 1 November 2007. It focused on the measurement of nutrients and of ocean CO_2 parameters, and also discussed the current status of available chemical reference material; particularly for nutrients references in ocean science were discussed. The participants agreed to start a collaborative program, called the International Nutrients Scale System (INSS), with the aim to establish global comparability and traceability of nutrients data.

The agreements at this workshop in Tsukuba 2007 marked an epoch in the history of nutrients comparability.

The 2009 INSS workshop in Paris is a follow-up meeting of 2007 workshop in Tsukuba to advance international collaboration in establishing global comparability of nutrients data in the world oceans.

1.2 HISTORY OF NUTRIENTS INTER-LABORATORY COMPARISON STUDY

This history of nutrients inter-laboratory comparison studies is based on several reports of previous intercomparison exercises. The histories of the first to fourth ICES exercises are derived from Aminot and Kirkwood's (1995) detailed report of the fifth ICES intercomparison. Histories of the fifth ICES exercise, the first and second NOAA/NRC inter-laboratory comparison study, MRI 2003 and 2006 intercomparisons are also summarized in this appendix.

1.2.1 FIRST ICES EXERCISE

The first intercalibration to include nutrients was an entirely Baltic affair in June 1965, when three research vessels met by private agreement in Copenhagen:

Aranda	Institute of Marine Research (IMR), Helsinki
Hermann Wattenberg	Institut für Meereskunde, Kiel
Skagerak	Royal Fishery Board, Gothenburg

Each ship contributed freshly collected bulk samples to the experiment, which were sub-sampled and analyzed on board each of the three participating ships on the same day. Oxygen, salinity, chlorinity, alkalinity, and phosphate were determined.

1.2.2 SECOND ICES EXERCISE

The second ICES exercise, carried out in 1966 under the auspices of the newly formed ICES Working Group on the Intercalibration of Chemical Methods, was still predominantly a Baltic initiative and consisted of two parts: Part I, Leningrad, during the 5th Conference of Baltic Oceanographers; and Part II, Copenhagen, at the 54th ICES Statutory Meeting.

Part I, Leningrad (May 1966)

The participating research vessels were

Alkor	Institut für Meereskunde, Kiel
Okeanograf	Institute of Marine Research, Leningrad
Prof Otto Krammel	Institut für Meereskunde, Warnemünde
Skagerak	Fisheries Board of Sweden, Gothenburg

The research vessels delivered bulk samples, which were sub-sampled and analyzed almost immediately for oxygen, salinity, chlorinity, pH, and phosphate.

Part II, Copenhagen (September 1966)

The list of interested parties continued to grow and, in addition to Baltic countries, Norway and the UK were represented. Research vessels delivered bulk samples and the various participants analyzed samples simultaneously in Copenhagen. The determinands of primary interest included not only oxygen, salinity, chlorinity, and phosphate, as in Part I (Leningrad) and the previous year's exercise (Copenhagen, 1965), but also nitrate, nitrite, and silicate.

The final report, edited by Grasshoff (UNESCO, 1966), makes no mention of nitrate or nitrite but some of those who were present confessed that these results were "too terrible to be included"! To be fair to those involved, 1966 was an early time in the development of heterogeneous cadmium-based nitrate/nitrite reduction techniques and some of the associated problems were presumably not fully appreciated at the time.

Evidently nitrate analysis had some way to go to achieve the reliability and ease of operation of the Murphy and Riley (1962) phosphate technique, but it is worth noting that inter-comparison work on phosphate so far had consisted of simultaneous analysis of freshly obtained subsamples by a small number of highly competent workers, in close contact with each other, exchanging calibration solutions, ideas, technical details, etc. Subsequent to the Copenhagen trial, Jones and Folkard (ICES, 1966) undertook a detailed laboratory examination of the individual methods used by the participants and, in their contribution to Grasshoff's report, they announced, "There seems to be no need for any further intercalibration in the determination of inorganic phosphate by this method."

Clearly this happy state of affairs could and did not last. Along came the autoanalyzer!

1.2.3 THIRD ICES EXERCISE

The third ICES exercise was organized by the ICES Working Group on Chemical Analysis of Sea Water under the joint auspices of ICES and SCOR and its official title, "The International Intercalibration Exercise for nutrients Methods 2", shows that it set out to be an ambitious project.

Samples were distributed in 1969–1970 and 45 laboratories from 20 countries submitted results, but the final report on the results of the exercise was not published for several years (ICES, 1977).

The time had come to study "nutrients" separately from oxygen, salinity, chlorinity, and pH, but with the awareness of problems arising from the instability of natural seawater samples, the organizers chose to use standard solutions that were prepared and distributed by the Sagami Chemical Research Center, Japan. [*Note added by Aoyama*: The standard solutions used in this exercise were Cooperative Survey of Kuroshio (CSK) standards, which are solutions in artificial seawater for nitrate, phosphate, and silicate and in pure water for nitrite.]

In this exercise, participants performed the analyses in their own laboratories but, despite being supplied (knowingly) with appropriate blank solutions for each determination, the overall accuracy, particularly for phosphate and nitrate, was disappointing.

The report concludes, "As methods did not diverge much, it is clear that variations must be sought primarily in the standardization procedures. The results will also aid participants in re-evaluating their analytical procedures by comparison of their methods with those that appear most satisfactory from this exercise".

The names of the participating laboratories were listed, as were the tables of results, but it was not possible to link them together. Hindsight suggests that this may have been counterproductive; we now suspect that there is no greater incentive for a laboratory to improve its performance than the knowledge that peer laboratories throughout the world are aware that it is producing poor quality data.

1.2.4 FOURTH ICES EXERCISE

Various "workshop" and multi-ship events following the ICES/SCOR exercise including nutrients Studies, but it was many years later (1988) before the ICES Marine Chemistry Working Group produced volunteers (Don Kirkwood, Alain Aminot, and Matti Perttilä) to organize the next large-scale intercalibration exercise, designated "NUTS I/C 4". This exercise did not set out to be worldwide, beginning only with laboratories in ICES Member Countries, but other laboratories who were interested in participating were not turned away.

The fourth exercise differed from the third exercise in three important respects.

1) The test samples were natural or near-natural seawater rather than standard solutions. (Strictly speaking, this made the exercise an intercomparison rather than an intercalibration.)
2) Participants were unaware that "blank" samples were included.
3) Anonymity was abolished. Participants were made aware from the outset that the final report would list identities of laboratories, results, and a means for any reader to contact them.

Sixty-nine laboratories from 22 countries submitted results and, thanks in some measure to the telefax machine, the final 83-page report (Kirkwood et al., 1991) was in the hands of participants within two years of the distribution of samples. Statistical treatment identified 58 laboratories consistent in phosphate analyses, 51 consistent in nitrate analyses, and 48 consistent in both phosphate and nitrate analyses, including a group of 12 whose results were especially close to the consensus concentrations.

1.2.5 FIFTH ICES EXERCISE

Due to the generally perceived need for more and better quality control in analytical measurement, a fifth ICES intercomparison exercise was carried out in 1993. A total of 142 sets of samples were distributed in 31 countries. Results were returned by 132 laboratories, 61 of which had participated in the fourth intercomparison and 56 of which were participating in QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe).

The distribution of laboratories was as follows:
UK (22), Germany (18), Sweden (13), France (11), Spain (8), USA (7), Norway(5), Ireland(5), Australia(4) Canada(4), Netherlands(4), Denmark(3), Greece(3), Portugal(3), Belgium(2), Estonia(2), Finland(2), Italy(2), Poland(2), Argentina(1), Bermuda(1), China(1), Faroe Islands(1), Iceland(1), Japan(1), Latvia(1), Lithuania(1), New Zealand(1), Qatar(1), South Africa(1), Turkey(1).

The method of sample preparation, autoclaving, for the fifth intercomparison imposed constraints that resulted in there being only two relevant determinands per sample (nitrate and nitrite in one series, and phosphate and ammonia in the other series).

A large volume of low-nutrients natural seawater was spiked with known concentrations of nutrients Salt. Although the concentrations in the distributed samples covered a greater concentration range than that in the fourth intercomparison, the concentration levels were representative of the Atlantic Ocean, 1–26 μmol L^{-1} for nitrate and 0.08–1.85 μmol L^{-1} for phosphate.

There have been no further ICES intercomparison exercises since 1993.

1.2.6 QUASIMEME

The European Union (EU) supported the QUASIMEME project between 1993 and 1995. Its aim was to develop a holistic quality assurance programme for marine environmental monitoring information in Europe. As a result of this pioneering project a marine network and laboratory performance studies have been established for most of the determinants measured in the marine environmental programmes for both monitoring and research purposes. The nutrients part of QUASIMEME was entirely based on the groundbreaking work of ICES experts and the principles and methodology described above were used. The project proved that laboratories which followed on a regular basis the learning programmes and the laboratory testing schemes improved the quality of their data.

After the end of the EU funding in 1995, the QUASIMEME scheme continued on subscription basis and now it is possible for any laboratory worldwide to participate. QUASIMEME results have been used to assess the quality of data submitted to the marine conventions for the purpose of assessing the quality status of the marine environment.

1.2.7 2000 NOAA/NRC INTERCOMPARISON

The test material distributed in this intercomparison was MOOS-1, a proposed certified reference material for nutrients in seawater (Clancy and Willie, 2004). The sample material was intended to be a certified reference material for silicate, phosphate, nitrite, and nitrate + nitrite. Participating laboratories were each sent two bottles of MOOS-1 and requested to perform duplicate analyses on each of the bottles. The prepared samples were sent to 36 participating laboratories. Thirty sets of results were returned.

The results of this intercomparison may, in several respects, have been compromised by sample homogeneity problems. The target standard deviation for measuring *p*-scores is too broad and does not reflect the measurement precision that can be attained.

1.2.8 2002 NOAA/NRC INTERCOMPARISON

A further intercomparison exercise was undertaken to assess the current capabilities of a group of laboratories to quantitate orthophosphate, silicate, nitrite, and nitrite + nitrate in a seawater sample. This was the second such exercise sponsored by the NOAA Center for Coastal Monitoring and Assessment (CCMA) and coordinated by the Institute for National Measurement Standards of the National Research Council of Canada. Two seawater samples — one from Pensacola Sound, FL, and a proposed certified reference material for nutrients in seawater (MOOS-1) — were distributed to 31 laboratories.

Twenty-four laboratories submitted data. Methodologies were not prescribed to the participants; however, all reported results were obtained using traditional colorimetric procedures. Generally, satisfactory agreement among participants was achieved, with results within 10% of the assigned mean values.

The results from this exercise suggested that the homogeneity problem identified in the first NOAA/NRC intercomparison exercise was overcome, although the orthophosphate data indicate a larger inter-laboratory spread of results than expected.
Results for silicate, nitrite, and nitrite + nitrate in the distributed seawater samples were acceptable for the majority of the participants and generally deviated <±10% from the assigned mean. All laboratories used methodology based on colorimetric principles.

1.2.9 2003 MRI INTERCOMPARISON

Autoclaved natural seawater was prepared for inter-laboratory comparison study samples. Sample homogeneity was confirmed by repeatability of measurement. Sets of 6 samples covering a concentration range greater than that in previous inter-laboratory comparison studies were distributed. The concentrations were 0–38 μmol kg–1 for nitrate, 0–0.9 μmol kg–1 for nitrite, 0–2.7 μmol kg–1 for phosphate, and 0–136 μmol kg–1 for silicate. A total of 18 sets of samples were distributed to 18 laboratories in 5 countries. Results were returned by 17 laboratories in 5 countries. Although consensus concentrations were obtained for the 6 samples, the standard deviations were 4.5 times and more than 10 times greater than those of the homogeneities for phosphate and silicate, respectively. For nitrate, the standard deviations were only about double the homogeneities. These results indicate that variability in in-house standards of the participating laboratories — rather than analytical precision — is the primary source of inter-laboratory discrepancy. Therefore use of a certified RMNS is essential for establishing nutrients data sets that can be compared across laboratories, especially for silicate and phosphate.

1.2.10 2006 MRI INTERCOMPARISON

Autoclaved natural seawater was used for an inter-laboratory comparison study for a reference material for nutrients in seawater in 2006, similar to the 2003 intercomparison exercise. Sample homogeneity was confirmed by repeatability of measurement and those for nitrate, phosphate and silicate were 0.2%, 0.3% and 0.2%, respectively. Sets of 6 samples covering a concentration range of 0.1 –42.4 μmol kg–1 for nitrate, 0.0–0.6 μmol kg–1 for nitrite, 0.0–3.0 μmol kg–1 for phosphate, and 1.7–156.1 μmol kg–1 for silicate were prepared. A total of 55 sets of samples were distributed to 55 laboratories in 20 countries. Results were returned by 52 laboratories from 19 countries.

1.2.11 2008 MRI INTERCOMPARISON

Autoclaved natural seawater was used for the next inter-laboratory comparison study for a reference material for nutrients in seawater in 2008, just as in 2003 and 2006. A total of 58 sets of samples were distributed to 58 laboratories in 20 countries. Results were returned by 52 laboratories from 19 countries.

Two of 6 samples used in 2008 I/C study were the same lots as used in the 2006 I/C study, therefore we can see internal comparability at each laboratory who participated both in the 2006 and 2008 studies as well as the international comparability of the nutrients data among the participating laboratories.

2. DISCUSSION

2.1 PLENARY TALKS

2.1.1 SESSION 1-CHAIR PERSON: ANDREW DICKSON

Two talks were presented in this session. David Hydes spoke on "How do we improve the comparability of nutrients measurements?" and Karel Bakker spoke "Comparison JRM vs. NIOZ used as Tracking Standards for nutrients data". In this session, Hydes point out that we need improvements in both internal (intra-laboratory precision) and external (inter-laboratory precision and accuracy). The use of tracking solutions which have a known concentration ("accuracy") and homogeneity (precision) could improve internal precision and external comparability. The results of the 2008 I/C study and results of using a tracking standard clearly show that using a tracking standard could improve intercomparability within cruise and RMNS within the cruise can make the link with other cruise data, improve external comparability, and give a good potential for improving precision within a cruise.

Karel Bakker showed his results from back correction using the NIOZ tracking standard and also the KANSO RMNS. His result was that by correcting using JRM as a Tracking Standard gave us slightly more consistent data compared to the NIOZ Tracking Standard. He also pointed out one advantage of RMNS is that the use of JRM is preferred because diluting in LNSW is not necessary anymore. For quality assessment a Tracking Standard is essential to check the data quality between runs, same for the Duplicates. Use of RMNS is a good way of calibrating the system, distributing the standards, this may be progress.

2.1.2 SESSION 2-CHAIR PERSON: DAVID HYDES

Four talks were presented in this session on how measurements at different times and by different laboratories can be both better coordinated and improved. Kenichiro Sato spoke on the "Comparability of Cruise-to-Cruise Using Reference Material for nutrients in Seawater, he was followed by Hidekazu Ota who described the "Development of RMNS (Reference Materials for nutrients in Seawater)", Anne

Daniel spoke about the "Use of low-nutrients coastal water for national inter-laboratory exercises" in France, and Michio Aoyama finished the session by describing his proposal for an "International Nutrients Scale System, INSS, in seawater"

The session clearly demonstrated that there is now considerable experience in the marine chemical community that can be used to bring about the needed improvement in the comparability of measurements within and between laboratories. Aoyama pointed out that particularly for studies of global change; improvements in the comparability and traceability of chemical data in the world's oceans are needed. Improvements in the comparability of CO2 parameters have been achieved by the use of Certified Reference materials (CRMs) and we are close to being able to do this for nutrients. A key aspect is to develop the needed degree of cooperation in the global community making these measurements and along with trust in the community that CRMs developed for nutrients will be reliable. The international collaboration is being built up by Aoyama through a series of inter-laboratory comparison studies that have been organised in 2003, 2006 and 2008. Aoyama saw this as being taken forward as an "International Nutrients Scale System (INSS) in seawater" to establish comparability and traceability of nutrients data in the ocean. This will be based on having the reference materials for nutrients in seawater certified by the National Metrology Institute of Japan (NMIJ) and data provided by the user community.

The most important step forward in producing RMs for the measurements of nutrients in seawater (RMNS) was described by Hidekazu Ota, and has been made possible by his company Kanso-Technos. In 2004 Technos built a facility dedicated to the production and bottling of sterile seawater. This facility contains a 'walk-in' Autoclave and a suite of clean rooms for sample preparation. Progressive developments have taken place in the autoclaving, and bottling and storage of the filled bottles. The RMNS's are made from natural seawaters and then mixtures of these seawaters can give the appropriate ranges of concentrations. Lots of up to 6000 bottles can be produced by the system at a time. Experience is such that we now know that the stability of early batches of RMNS produced by Technos has been maintained for five years, when stored in normal environment (i.e., at room temperature).

The materials produced by Technos have been used as the basis of the inter-laboratory comparison study organised by Aoyama in 2006 and 2008 and have also now been used extensively on Japanese cruises carrying deep sea hydrographic work in WOCE related programmes. Kenichiro Sato reported on these results from WOCE re-occupation cruises on the R/V Mirai to look at the decadal change of the general circulations of the ocean. To obtain improved comparability between cruises, RMNS have been used since 2003. RMNS's are measured at all stations to keep the comparability through the cruise, and the use of RMNS's with assigned values on all the cruise has enabled the comparability of cruise-to-cruise observations, with data to be established going back to 2003. Comparison of the data from cross-overs between cruises shows much closer agreement when the RMNS materials have been used compared to the results of cross-over comparisons determined in the data analysis work such as the CARINA project discussed later in the day. Interesting from a geochemical point of view is that the use of the RMNS materials produces a lowering in the apparent N:P (Redfield) ratio and a well defined transition in the value between intermediate and deep waters.

At national level Anne Daniel reported on the work that has been led by IFREMER to improve the comparability of the 30 laboratories in France making measurements of nutrients in coastal waters and estuaries. This has been done on the basis of the preparation of detailed guidance notes for the laboratories that then follow an agreed set of methods developed by IFREMER. A key role in this work is played by the periodic determination by the laboratories of comparison materials prepared by the pasteurisation of seawater samples. Using 'aged' natural seawater containing low levels of nutrients Separate solutions are prepared containing (i) nitrate and nitrite (ii) phosphate and silicate, and (iii) ammonia. After pasteurisation these solution have been found to be stable for more than one year.

2.1.3 SESSION 3-CHAIR PERSON: MALCOLM WOODWARD

Initially this was scheduled to have 3 presentations but due to the stormy weather having closed Paris Charles de Gaulle Airport on Monday 9th, unfortunately Toste Tanhua was weather-bound in Hamburg and so did not arrive until late. His talk was re-scheduled to a later session so this session had only 2 presentations.

Steven van Heuven from the University of Groningen in the Netherlands, thus gave the first presentation titled, 'nutrients in CARINA'. CARINA is the 'Carbon in the North Atlantic' project, which ran from 2005-2009, as part of the EU IP CarboOcean. The goals of CARINA were to collect and salvage recent and historic CO2-related datasets and to assess and ascertain the quality of this data and to subsequently attempt to generate an internally consistent data product.

The set of data investigated consists of 188 cruises, over 15,000 sampling stations, a quarter of a million actual samples and 2.5 million measurements. The global coverage and cruise tracks demonstrated the international effort that this dataset represents. The data were divided into quality controlled and non quality controlled with the nutrients coming into the QCed section, along with oxygen, DIC, total alkalinity, pH, CFC's 11 and 12, and salinity. The project was well advanced with all quality control complete and the final product nearing release, along with almost 20 manuscripts being prepared.

The procedure of the quality control process was discussed, for example all outliers were discarded and then a second iteration was carried out to determine inter-cruise offsets and biases, and adjust the data accordingly. It was pointed out this was carried out very cautiously. Examples of cross-over data were shown for nitrate, silicate and phosphate data sets, and also the errors in the data were reviewed, showing improvements over the last 25 years for the nitrate, phosphate, DIC and silicate standard deviations, and the lowering of the errors with the offsets between cruises.

The conclusions were that the originally reported data were generally below WOCE-quality because of analytical inaccuracy and imprecision, and occasionally drift between stations (assuming little natural variability between deep water masses). By applying the corrections (determined through inversions according to Johnson, J. Atmos. Oceanic Technol, 2001) the data quality is improved to the point of being classifiable as 'WOCE quality', with all errors lowered accordingly. The conclusions

also echoed the sentiment of the meeting in that a RM for nutrients would have been a great help in ensuring nutrients data sets were more reliable and consistent in quality.

Florence Nedelec from the Laboratoire Environment et Resource de Normandie, gave the second presentation about the application of nutrients data for the assessment of eutrophication and management in the Normandy coastal waters. This project is being instigated in response to European Union directives resulting from the OSPAR convention of 1992. The aim of that convention was stated as being to protect and conserve (or restore) ecosystems and biodiversity of maritime areas under the influence of adverse human activities. The developed strategy was to achieve a healthy marine environment where no eutrophication was occurring by 2010, and with a 50% reduction in nitrogen and phosphorus inputs. The assessment parameters were set out into 4 categories, the degree of nutrients enrichment, the direct effects of this enrichment, the indirect effects, and other possible effects due to nutrients enrichment like increased prevalence of algal toxins and DSP/PSP on mussels. A more recent European framework directive was discussed which had the aim to achieve a 'good status' for all waters by 2015 and also to prevent further deterioration in the environment. The parameters and methods for assessment were highlighted, with discussions concerning the French nationwide efforts in this area, which was a co-ordinated plan between all the laboratories within the IFREMER structure, and also with 5 overseas departments. Water quality assessment parameters were discussed and the need for a European inter-calibration group was highlighted. Nutrients results were shown for a gradient out to the coast waters with nutrients concentration gradients and the point sources. They also pointed out the need for a CRM for the inter-comparison exercises and the development of the INSS was seen as being an important step forward in achieving a reliable RM.

So in the overall context it is good to see two sets of research investigating data and data sets both highlight the urgent need for Reference Materials for nutrients which is the overall outcome of the INSS programme.

2.1.4 POSTER SESSION-CHAIR PERSON: AKIHIKO MURATA

This section was arranged so that we could have enough time for discussion on technology. There were 5 poster presentations. In the followings, each presentation is summarized briefly.

Aoyama reported preliminary results of 2008 RMNS inter-laboratory comparison study. 38 of 58 participating laboratories also joined the comparison study in 2006. The laboratories presented a consistent result for samples of a same lot in the two time periods, implying that the laboratories have kept a within-laboratory consistency of nutrients measurement. This means that we can correct between-laboratories differences of nutrients measurements by using RMNS. However, there remains a problem related to analytical method, probably due to non-linearity of instrument response.

Kawamoto and Coverly presented an automated method for ammonia as follows: First, EDTA buffer is added to prevent seawater from producing hydroxide. Then NaOH/EDTA is added to convert NH4 ion to NH3 gas. With a PTFE

membrane, NH3 gas is dialyzed into an acid recipient. Ionized NH4 in an acid recipient is analyzed by the indophenols blue method. The presented method improves sensitivity by 5 times.

Dissolved oxygen is one of the most frequently measured properties on board a research vessel. However, no RM exists for dissolved oxygen. This situation makes it difficult to compare data obtained by different laboratories. Mitsuda et al. attempt to produce RM for dissolved oxygen based on technique used for non-toxic RM for DIC. From homogeneity test of RM, they conclude that development of RM for dissolved oxygen is possible.

RM has to be stable as long as possible. Sato and Aoyama checked stability of RMNS for up to 6 years, and demonstrated that concentrations of nitrate, phosphate and silicate in different lots of high, middle and low concentrations were stable enough as RM.

Weigelt-Krenz et al. presented results of inter-laboratory comparison among 6 German laboratories. The main purpose was to compare different conservative techniques (deep freezing and poisoning with HgCl2) and different analytical methods. In spite of those different conditions, inter-laboratory variability was generally less than 10% for nitrate+nitrite, nitrite, silicate and phosphate. However, results of ammonium showed variability ranging from 0.5% to 45%, probably related to methodological problems for storage and/or analysis.

2.1.5 SESSION 4-CHAIR PERSON- MICHIO AOYAMA

Four talks were presented in this session on carbonate system reference materials and reference materials for dissolved organic matter.

Andrew Dickson spoke on the “reference material for seawater pH measurements”. He pointed out the significance of pH for the study of oceanic CO2 system as well as another parameter, ideally Ct. His approach would achieve the overall uncertainty to be about 0.002 in pH. There are remaining tasks such as adjustment of certified values to harmonize the pH of the buffer, with pH measured using m-cresol purple. His achievement led to a discussion about the idea of an inter-comparison experiment for pH using natural seawater and tris buffer.

Akihiko Murata spoke on the “non-toxic reference material of DIC”. There already exists RM for DIC and TA, which possesses long-term stability enough for a practical use, and is certified simultaneously in one bottle for the two parameters by Prof. A. G. Dickson of Scripps Institute of Oceanography. The CRM was used during the WOCE and JGOFS programs in the 1990s. As a result, comparability of data for DIC and TA has become considerably improved in recent years. His group uses autoclave technology at KANSO for preparing nutrients reference material, as presented by Ota et al. and Aoyama in this workshop, and also to develop a non-toxic reference material for DIC. This development is close to success. Andrew Dickson offered to certify the newly developed non-toxic RM for DIC and agreed to more collaboration between his laboratory and Japanese group. From the viewpoints of safety and being environmentally friendly, it is desirable to avoid use of toxicant

substances. Therefore this progress and collaboration would contribute to the international community and its use of these reference materials.

Jonathan Sharp spoke by video and discussed via a telephone connection because he was not able to attend the Paris meeting. His talk was on "DOC/DON reference material". His group had demonstrated that they can improve quality of DOC analyses through reference material use. For DON analyses, they demonstrated the need to improve DON RM's and they are awaiting results of a DON reference exercise in 2008, in which they prepared 3000 ampoules and sent them to 16 labs. He also evaluated the reference material for nutrients prepared by KANSO, as reference material of DOC and DON. In his report, DOC values of RM-BF and RM-BG looks good, however, some NH4 contamination was suspected. It was suggested that his group and the INSS group could collaborate more in the future to produce multi-use reference.

Takeshi Yoshimura spoke on "RMNS for DOP analysis". He observed that homogeneity of DOP concentrations in PP bottles is not good enough, and some problems may occur in aluminum bottles for DOP measurement, while the homogeneity of DOP concentration looks good.

Throughout this session, there was the hope expressed to be able to use INSS reference material as a DOC, DON and DOP reference material in the future. We also see progress on non-toxic DIC reference and these will also be available in the near future.

2.1.6 SESSION 5-CHAIR PERSON: PATRICK ROOSE

Five talks were presented in this session. Stephen Coverly spoke on "Quantifying, evaluating and recording instrument- and method-related performance parameters in a segmented-flow analyzer". In his talk, he emphasized the importance to monitor the many performance parameters during the analysis. In the discussion, he also emphasized the importance of training with the analyzer. Malcolm Woodward spoke on "Ammonium analysis: search for the holy grail". In wide areas of the world's oceans phytoplankton productivity is limited by the availability of nitrogen. The surface waters and the surface mixed layers of many temperate oceans typically are greatly depleted of dissolved inorganic nitrogen species (ammonia, nitrate and also phosphate). In order to understand the cycling these nutrients, particularly in the nutrients deplete, oligotrophic offshore waters like for example the Atlantic gyres, we need the ability to not only detect these species at the nanomolar concentrations they are found in but also to be able to make reliable measurements. This has been a major challenge in marine nutrients chemistry to develop robust and reliable sea-going analytical techniques, and analysts, for working in often extreme oceanic environments. Recent years have shown developments in the analytical capabilities for ammonium and other nutrients, but despite being able to analyse these in often nanomolar concentrations it is also absolutely imperative that we have sampling and handling techniques similarly developed and checked out in order to be able to report results in complete confidence. He also point out on big question for ammonium measurement as follows.

What is our baseline ie: our zero?
Ammonium has contamination sources from just about everywhere
A stoppered glass bottle with surface seawater sample:

In 2008 I/C study for ammonia, taking all 12 labs results then up to 50% variations in the results were shown and a couple laboratories had shown big variations. In the discussion, Aoyama pointed out that KANSO RMNS had not prepared for ammonia at this moment. However, it might possible to improve current RMNS to fit for ammonia. Patrick Roose also pointed out that ammonia RMNS by QUASIMEME also show higher variability.

Günther Nausch spoke on "DOP measurements in the Baltic Sea – methodological aspects and results".

Kazuhiro Misumi spoke on "Nutrients distributions simulated in an Ocean General Circulation Model". His model was based on the BEC (Biogeochemical Elemental Cycling) model of the NCAR Community Climate System Model. Since models are developed referring to the metrics based on observed data, precise observational nutrients data will contribute to further model improvement. He pointed out that to improve the processes incorporated in models, direct comparison between in situ data with simulated results is important.

Toste Tanhua spoke on "Importance of accurate nutrients measurements for Cant inference". In his talk, he emphasized importance of accurate nutrients adapt on anthropogenic carbon estimation because anthropogenic carbon, Cant, can not be measured directly. It has to be calculated by some kind of calculation and some of these calculations do involve nutrients measurements. Nutrients values tend to be high in old waters, where the Cant ant signal is small. Therefore even a relatively small bias in nutrients data can bias the calculated C Cant ant significantly in a region where the Cant concentration is normally low. Even if the absolute difference in Cant is small, there is a large volume of low/high nutrients waters in the world oceans. Thus, biased nutrients data will make a difference to the inventory calculations.

2.2 TOXIC AND NON-TOXIC RMS FOR CO2-SYSTEM PARAMETERS
CHAIR PERSON: AKIHIKO MURATA

2.2.1 INTRODUCTION

The ocean plays an important role in reducing impacts of global warming, and it is estimated that it absorbs about 30% of CO2 emitted into the atmosphere by human activities. One of the methods which demonstrate uptake of CO2 by the ocean is to detect increases of CO2 dissolved in seawater on a global scale. This is a certain approach, but could never be attained without the international cooperation of oceanic observations. In fact, global survey efforts in the 1990s were conducted under the international framework of the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS). In these activities, the most important issue was to establish a reference material (RM) for CO2-system parameters such as

dissolved inorganic carbon (DIC), total alkalinity (TA), etc., which can improve comparability of data collected by many laboratories.

As well as many other chemical properties, values of CO2-system parameters change considerably due to biological activity. Thus toxicant substances are usually added into RM solutions. However, from the viewpoints of safety and being environmentally friendly, it is desirable to avoid use of toxicant substances. On this account, development of non-toxic RM is rationalized.

2.2.2 TOXIC RM FOR CO2-SYSTEM PARAMETERS

There already exists RM for DIC and TA, which possesses long-term stability enough for a practical use, and is certified simultaneously in one bottle for the two parameters by Prof. A. G. Dickson of Scripps Institute of Oceanography. The CRM was used during the WOCE and JGOFS programs in the 1990s. As a result, comparability of data for DIC and TA becomes improved considerably.

The CRM is produced from natural seawater by equilibrating seawater with laboratory air, and sterilized by a combination of filtration, ultra-violet radiation and addition of mercuric chloride. Then seawater is bottled in 500 mL borosilicate glass bottles sealed with greased ground glass stoppers. Up to now (March 2009), 93 batches are certified for DIC and TA.

2.2.3 NON-TOXIC RM FOR CO2-SYSTEM PARAMETERS

The non-toxic RM is produced based on the technique applied to reference materials for nutrients in seawater (RMNS), which are non-toxic and have been already successfully used as a reliable RM in shipboard observations. This idea comes from that the sterilization technique effective for nutrients. It should also be effective for CT. That is, seawater is sterilized by high temperature and high pressure treatment by an autoclave. The sterilized seawater is bottled in aluminium bottles (300 ml or 500 ml) and vacuum-sealed in aluminium bags.

The non-toxic RM is still under development, but shows little bottle to bottle differences. The development is now investigating a preservation experiment. Up to now, concentrations of CT have remained unchanged for about 90 days.

2.2.4 FUTURE PLANS

In a sub-group meeting of the workshop, a grant-in-aid for scientific research related to RM, which is a proposal for the Ministry of Education, Culture, Sports, Science and Technology in Japan, was introduced. Furthermore, future plans were discussed for an RM of CO2-system parameters, which will be based on the current technique of RM or CRM production. As a result, the following were agreed: (1) designing an inter-comparison experiment for pH using natural seawater and tris buffer; (2) improving the non-toxic RM for DIC and TA, and investigating it being certified if possible; (3) using experimental aluminium bottles for toxic CRM's. These

activities will be able to be conducted fully if the grand-in-aid is approved, but will be reduced if not approved.

2.3 EXPAND RM FOR DOC, DON AND DOP REFERENCE - CHAIR PERSON: TAKESHI YOSHIMURA

Eleven participants discussed the expansion of RMNS for DOC, DON, and DOP analysis, and confirmed that we require appropriate RMs for DOM analysis. At present, QUASIMEME has provided an inter-comparison program including total N and total P for 5 years among the EU community. However, the program is not a system for providing RMs with consensus values, so we cannot decide whether our analytical results are comparable in the international community compared with other DOM analysts. Although Hansell's laboratory in the University of Miami provides RMs in 10-mL glass ampoules with consensus values of DOC and total dissolved N (TDN) which are suitable for high temperature combustion analysis, some laboratories require a relatively large volume to complete the analysis and moreover RMs for total dissolved P (TDP) or DOP are not available. We concluded that we need to create appropriate RMs for DOM analysis.

An issue regarding DON and DOP analysis is that we cannot measure them directly but we have to estimate their concentrations as the difference between TDN and dissolved inorganic N (DIN), and TDP and PO4. The background DIN and PO4 usually are very high in seawater, so the uncertainty of DON and DOP estimation can be large. Thus a high priority is to create RMs with zero inorganic nutrients and significant amounts of DOM.

Post phytoplankton bloom surface waters can be appropriate for the RMs. Subtropical surface water also is a candidate. Second, RMs which are depleted both in inorganic nutrients and in DOM would be useful. However we can not find such seawater all over the world. We may find very low TN/TP water around the Canary Islands in the Atlantic and around Guam in the Pacific. Presentations in this workshop by John Sharp and Takeshi Yoshimura conclude that the present RMNS are not necessarily suitable for DOM reference materials. However, we have to make an effort to improve the RMNS for appropriate DOM reference materials.

2.4 CFA TECHNOLOGY - CHAIR PERSON: MALCOLM WOODWARD

Initially this was to have been a three session discussion about various aspects of CFA technology, however with the overwhelming interest in the rewriting of the nutrients manual that session was extended to allow more time for discussions with all participants, so the CFA technology discussion was reduced to just one session.

After canvassing for topics the one agreed with all was to discuss the Matrix effects that can affect the results, when analysing for nutrients. An overview was presented by Stephen Coverly as a small presentation and discussions continued from this.

The Matrix effects discussed were split into:

i) the salt effects on the optical signal; which are the schleiron effect due to different refractive indexes of the samples and wash waters, and also the refractive index blank which depends on the refractive index of the water being analysed but is not influenced by the flow of the liquid.

ii) The salt effect on the reaction rate or reaction end point, and

iii) other effects like the matrix absorbance, fluorescence and light scattering.

Diagrams and overheads detailed each of these effects and how they influenced the segmented flow analyser flow-cells and the sort of computer outputs were generated from these.

Interesting discussions were made around these effects and to what actions different laboratories were doing to ensure they properly assessed and made allowances (corrections) for these effects on their own particular analytical techniques. Particularly interesting was that the majority of opinion was in using DI / Milli-Q water as the 'baseline' or zero, with one lone voice using artificial sea-water, however this did still appear to give good results within the last INSS exercise last December.

But the general opinion was that DI was the probably the best way to run baselines rather than artificial or low Nutrients Seawater ones.

The discussions showed a wide variation in how different people dealt with the problems and it was asked that if possible then Seal analytical would investigate the possibilities of incorporating running the refractive index blanks as part of the normal software programme within the AAIII and Quattro analysers. Whether other suppliers could be persuaded to do likewise is unknown.

The refractive index blank was discussed and measures to reduce it were highlighted,
salt effects vary depending on the analytical methods used and between the species analysed, with generally ammonium agreed as having the greatest salt effect, various people discussed their own various differences, again all because there is not one method that everyone uses around the world, which of course can be safely said will never happen.

The summary slides gave details of the matrix effect and the corrections required, with the advantages and disadvantages for each option.

A good discussion session with a lot of discussion from the floor and hopefully a session that highlighted an area that is very important when ensuring the correct reporting of nutrients concentrations.

2.5 NUTRIENTS MANUAL UPDATE - CHAIR PERSON: DAVID HYDES

The "International Workshop on Chemical Reference Materials in Ocean science" organised by Michio Aoyama in Tsukuba, in Japan in late 2007 agreed that in order to promote 'best practice' in the measurement of nutrients in seawater, along side the use of RMNS's, then a rewrite of the WOCE manual produced by Gordon et al. (1993) should be undertaken. David Hydes agreed to lead this work and looked

forward to the assistance of many of those present at the meeting. Early in 2008 the 'Go-Ship' community agreed to a general rewrite of the WOCE manuals and the rewrite of the nutrients manual is now being done as part of that Go-Ship activity.

In Paris, Hydes reported that working with Aoyama a decision had been taken to follow the model of the manual prepared by the carbonate chemists (Dickson et al., 2007). The result is a core descriptive manual associated with set of individual Standard Operating Procedures (SOPs) for the nutrients measurements (NSOPs). Andrew Dickson kindly agreed to provide the text for several of the carbonate SOPs for which the bulk of the procedure is similar.

Hydes reported that prior to the meeting the core manual had been uploaded to the Go-Ship manual web site (http://cdiac3.ornl.gov/hydrography) from where it can be downloaded for review. During the meeting those NSOP ready for review were up loaded to the site. Progress of the different sections was discussed. The core manual is now complete except for small addition to the section on the use of RMNS solutions as tracking standards and discussion on the detection of likely size of errors resulting from the fitting of linear calibration lines to non linear data. Karel Bakker, Susan Becker, Kenichiro Sato and Michio Aoyama agreed to provide input in these areas. The subject of the most appropriate lay-out of the sample table used when running a gas segmented flow analyser (SFA) was raised and Stephen Coverly (SEAL analytical) agreed to provide input on this.

Progress on the individual NSOP's was then considered. The final list of NSOP's agreed by the meeting was not altered from that listed in the core manual put up for review before the meeting except the content NSOP -15 would be moved elsewhere :-

Water sampling and sample storage for nutrients
Low level nutrients - water sampling and sample storage
Example SOP for CFA operations at sea
Gravimetric calibration of volumetric flasks and pipettes
Preparation of calibration solutions
Recommendations for CFA sample table layout including use of duplicate, tracking and RMNS samples
Establishing the linearity of calibrations
Procedure for use of tracking samples including end of cruise adjustment of data
Procedure for use of tracking and RMNS samples including end of cruise adjustment of data
Determination of true blank value
Example ship board cruise and metadata report
Applying air buoyancy corrections
Preparation of control charts
Statistical techniques used in quality assessment
Information "SOP" preparation of RMNS for a particular area

NSOPs 1 to 3 were put up on the website for review. For NSOP-4 Dickson has provided Hydes with the appropriate CO2 documents and for NSOPs 12 to 14. NSOP 5 on the preparation of standards has also been transferred to website. This is largely based on the recommendation of Aminot et al. (2009). NSOP-6, recommendations for

CFA table layout was discussed and Steven Coverly agreed to produce a draft for discussion. Earlier in the meeting Aoyama had shown that his analysis of the data returned in the 2006 and 2008 inter-comparison exercises suggested the some of the labs had errors in the results of their mid range samples consistent with the calibrations they were applying being in appropriate. Susan Becker agreed to lead the task of generating a NSOP-7 on the detection of non-linearity in calibration data and the choice of appropriate calibration routines. The need for two NSOPs (8 and 9) on the use of an "in-house" and RMNS as tracking standards was discussed. Karel Bakker agreed to work on these taking the draft version of NSOP-8 provided by Hydes as starting point. Bakker also agreed to work with Roger Kerouel and Anne Daniel on NSOP-10 "Determination of true blank value". Practices differ widely between laboratories for how this is done, and the choice of methods is now wider as the improved optics of the newer designs of CFA equipment make it possible use pure water as the "wash solution".

The aim for NSOP-11 is to produce an example cruise meta-data report. It was agreed that it is critical that as the use of RMNS solutions is taken forward progress needs to be made in meta-data reporting so that it is known:- precisely how the analyses were calibrated, what use was made of RMNSs, what the precision of the individual measurements was and how well this was maintained during a cruise. It was agreed that it was also important concentrate on reporting "useful" information. Hydes agreed to continue working on his draft of this NSOP.

NSOPs 12 to 14 can largely be base on the corresponding CO2 SOPs. However it was felt that particularly NSOP-14 should be looked at and expanded to include and explain the current thinking on the best use of terminology such as "accuracy" and "precision". Patrick Roose and Olivier Grosso agreed to review NSOPs 13 and 14 and revise them as appropriate particularly with advice on the best way of presenting the analytical uncertainty in our measurements.

The meeting agreed that for writing of future papers that will include nutrients data that has been measured relative to RMNSs it was important that there should be standard reference that describes the manufacture of the RMNS materials. Aoyama agree that he and Hidekazu Ota would provide the appropriate text and that this would be included in the published version of the nutrients manual.

2.6 SHORT-TERM STABILITY EXPERIMENT–CHARACTERIZATION OF RMNS
CHAIR PERSON: MICHIO AOYAMA

It was decided by the RMNS co-ordination team to carry out the stability testing of the RMNS between 2009 and 2011.

Following the global INSS inter-calibration exercises in 2006 and 2008, using the RMNS samples, it is the intention to now check the stability of the RMNS samples over the longer time period of 2 years. Laboratories will carry out analyses of the provided RMNS samples according to the protocols that follow.

Plan for a global stability test
Period: every 6 months for three years from March 2009 to September 2011

Total number of measurement: 6
Number of bottles of RMNS: n=2, with triplicate sample measurements, therefore the total number of samples producing data would be 6.
Number of lots of RMNS: n=3 at ratios for low, medium and high concentrations.

List of participating laboratories:
Ifremer, Brest, France
AOML, NOAA, USA
PML, NOC, UK
SIO, USA
NIOZ, The Netherlands
JAMSTEC, Japan
BIO, Canada
NOC, UK
MUMM, Belgium

2.7 USAGE OF NUTRIENTS DATA AND CARBONATE SYSTEM DATA IN OCEANOGRAPHY:

CHAIR PERSON: TOSTE TANHUA

Questions asked:

- What are the uses of nutrients and carbonate system data?
- How accurate/precise does the measurements need to be?
- Will this be dependent on what we want to do, or should we just do the best we can and see what we can use the data for?
- What data shall we be collecting? NO3, NO2, SiO2, NH4, DIC, TA, pH etc?

Some usages of nutrients and carbonate system data:
Anthropogenic Carbon calculations
Decadal changes in nutrients/carbon content/inventory
Changes in biological activity / re-mineralization
Acidification, magnitude
Water mass analysis, i.e. OMP
Changes in Redfield ratios
Nitrogen fixation / Denitrification

Points raised during the discussions:

- We know that even if the precision of the individual labs are within the WOCE standards (2%), the accuracy of the measurements is significantly lower. We know this from inter-calibration exercises and consistency analyses (i.e. GLODAP and CARINA).
- If we want to be able to detect decadal changes in nutrients content, we need to improve and be accurate to better than 0.5% since decadal changes are in the order or 1% per decade (reasonable numbers for accuracy needed to detect a 1% change still to be calculated correctly).
- Accuracy of 0.5% seems to feasible with the use of RMNS
- Without RMNS we are hard pressed to achieve better than 2% accuracy.

- An offer to compare stock-solution standards for silicate by the NIOZ group is welcomed, and will be helpful to improve inter-lab consistency.

2.8 DISCUSSION ON INTERNATIONAL NUTRIENTS SCALE SYSTEM (INSS) CHAIR PERSON: MICHIO AOYAMA

SUMMARY OF PRESENT STATUS OF INSS:

Ongoing issues:

- NMIJ is working to certify RMNS within 2009.
- Manual of nutrients measurements would be updated in 2009.
- Global stability test of RMNS, 2009-2011 by 10 core laboratories. Commencing April 2009:
- Open INSS web page:
- Silicate stock solution experiment at NIOZ to begin in spring 2009.
  David could provide bottles used at OSI before summer. Highest diluted silicate concentration used for calibration added as the information.
  Karel at NIOZ would make protocol.
- Research fund proposal, JPY147,000,000, EURO1,2000,000, for INSS in 2009 – 2013 was sent to Japanese government by some of organizers of this workshop.

Note: Our proposal was not approved in May 2009. We will send it again in fall 2009.

Questions asked:

- National key labs working to improve comparability of nutrients in seawater. Do they want to have RMNS from INSS group?
- Do we continue RMNS inter-laboratory study in two-year intervals?
  This was general agreed by the participants.
- We need to clarify the goals for these inter-laboratory studies. Before we do the inter-laboratory study, we need a proficiency test (PT) and the new protocol. Our goal might be to investigate reaching a higher level of accuracy. How can this be reached.
- We still do not have clear idea what figures are relevant to the accuracy.
- Will CRM assigned by NMIJ be completed before this study? If inter-laboratory study will be before 2010, CRMs will not be assigned yet.
- Increase in reproducibility in each laboratory should be investigated.
- Uncertainty of CRM by NIMJ might be larger than what we want to achieve.
- Inter-laboratory study forces a lot of work to all of us, is it worth to continue? Inter-laboratory study would give information on the state of the laboratory that is participating.
- Follow the protocol, and flatten out the curve.
- Distribution of RMNS to community, how?
  To CLIVAR cruises - yes
  RMNS inter-laboratory comparison study - yes
  National key laboratories working to improve comparability of nutrients in seawater - yes?

- IAPSO Salinity standard are produced about 2000-4000 bottles per year.
  If more people use RMNS, we also need 2000-4000 bottles per lot.
- For salinity standards, only 1 level standard is used. However, nutrients measurement need at least 3 levels of concentration to handle calibration curves to avoid non-linear problems.
- How many bottles of RM are needed for a cruise? What number would be helpful?
  NIOZ: need one bottle per every station. For Atlantic it may be need less.
  1 bottle per station would be better. At least at the initial stage.
- During a cruise we do 4-5 stations per day, therefore, 1 set per day for a cruise would be helpful.
- Is RM used to calibrate the instrument?
  Possibilities are open, but to hesitate to use for calibration at this stage.
  It might depend on the sea area you are working.
  We need four levels of RM as calibrants.
  We cannot use RM every time.
- Now RMNS can cover 90% of the world ocean in terms of volume.

Some state that they want to expand RMs in nanomolar nutrients concentration levels.

Points raised during the discussions:

1. Community will continue to collect resource seawater to make RMNS and CRM.
   Woodward hopes to collect for the next 3 years Atlantic seawater during the Atlantic Meridional Transect (AMT) cruises in October/November. As long as no sauna!
   JAMSTEC Mirai cruise: not next year, but next three years to north pacific.
   Not possible to collect seawater. Pacific cruise 2009 – 2011 but during this time frame it is possible.

2. In France, we do not know if we will continue inter-lab study. The labs are in good levels thus 2-3 years it might be reduced.
   What is the state of CANADA and USA?
   State of MOOS-2 material? CANADA is planning to produce MOOS-2 which might be near "medium" if they produce it.

3. Ammonium matter:
   We need to do some to expand RMNS to ammonium.
   Need to improve method of measurements of ammonium.

4. Idea of price of RM to buy them for survey. 10,000 yen. Not cheap!!
   If the proposal is passed, then 10000 bottles will be handed to you however, the data must be available with appropriate reported format.

5. Publish a workshop report as a publication of IOC-UNESCO within 1 year.
   Possible contents:
   Summary of this workshop by organizers
   Brief description of nutrients manual by Hydes and Aoyama
   Review of current status of our RMNS by Aoyama, Sato and Ota
   Review of current toxic and non-toxic carbonate system RM and future plan by Murata and Dickson
   Review of DOM RM by Yoshimura and Sharp

Summary of 2003, 2006 and 2008 RMNS inter-laboratory comparison study by Aoyama and Roose
Plan of stability test by Woodward
Review and current status of CRM for nutrients by Hioki, NMIJ
Cant and nutrients, importance of accurate nutrients measurements by Tanhua
Review of issues of CFA technology by Woodward and Coverly
National inter-laboratory exercises by Daniel

2.9 GENERAL DISCUSSION CHAIR PERSON: ANDREW DICKSON

2.9.1 SHOULD WE SEEK TO FORM SUCH A GROUP UNDER IOC AND/OR ICES?

Goal(s) of working group:

- Improve methods for autoanalyzers
- Reduction in uncertainty of measurement (for the community) Choice of target for uncertainty [minimum quality criteria]
- Are there problems other than instruments?
- Sampling/contamination concerns (especially for low level)
- Concern about quality of silicate data (calibration problem?)
- Inclusion of low-level techniques?
  Practical for marine nutrients analysis or blue water nutrients analysis (last 10 years)?
  Potential for all fields if measurements improve?
  Why: descriptions in scientific goals: Why did you choose 1%?
  Some practically: looking for efficient way
- Development of best practices/improved instruments

2.9.2 STRATEGY (IES) FOR ACHIEVING THAT GOAL?

- Promotion of development and use of reference materials (need for "low concentration nutrients" material?
- Promotion of best practice. More consistency in methods
- Try to clarify why we are having the problems we know about.
- IC/ run effective proficiency test – PT (e.g., QUASIMEME model with results and workshop?)

2.9.3 WHAT ACTIONS SHOULD WE TAKE?

Scientists can check their analysis (improve on their own)
Most effective way was to have workshop, invite analyst after PT,
To figure out the cost of this working group, we need to know what we are planning to do.
If there is PT how many can participate (many)?
If their workshop after how many can you pay your way to participate? (less number)
First: do participants think it is good idea to have a working group? Yes: good idea

Two areas: What have you achieved? (say two - three year time frame)
Flow charts to improve methods?
Real zero low Nutrients Seawater. Production of RM at this level as well.

2.9.4 PUBLICATIONS

Short time frame - circulation for comments

Workshop report will be published as follows.
Summary of presentation, text from working group, decision made in the discussions.

Nutrients measurement manual will be published as follows.
Manual: final draft web for final review in -autumn 2009.
Draft internal review end of this year

We plan to publish a book as follows.
The book is not for scientific literature, but it may be useful. Possibilities include

- Preparation of reference materials (very valuable information to be recorded)
- Stability/ homogeneity on RMs
- Assignment of values to RMs (work to assign values) How should/will this be done?)
- Effective use of RMs for QC (always limited results, not practical, sufficient RM that can be used for every opportunities relative to the cost)
- "secondary level quality control" , consistency checks(cruise crossovers, MLRs)
- Can we make this unnecessary by starting to use CRMs?
- Quality control definition of analyst (avoid getting rid of data they don't like) and oceanogeologist (rid of data that is "outlier")?
- Schedule of publication of the book is 18 months from today, by August 2010. Therefore, we need to complete the draft of the book within 12 months.

2.10 CLOSING SESSION - CHAIR PERSON: DAVID HYDES

Dr. Hydes asked to each chair to summarize our discussion in the closing session. These are appeared at chapter of summary and action items in this report.

At the end of the workshop, all participants paid their condolences on the death of Dan Wruck who was our good friend and collaborator.

3. CONCLUSIONS

Participants of this workshop have agreed that by establishing the INSS (International Nutrients Scale System), the comparability and traceability of nutrients data in seawater can be ensured. Thus, not only the study for nutrients in seawater itself will move forward, but also the amount of accumulated anthropogenic CO_2 will be accurately evaluated. Both are essential for the study for global change.

Participants also agreed that by publishing a new manual for nutrients analysis, the analytical methods with the greatest accuracy which is currently being achieved by our community can be shared with the remainder of the world science community. These decisions are expected to contribute to the improvement of the studies of nutrients in seawater, as well as the study of both of global warming and ocean acidification, due to increased emission of anthropogenic CO_2.

To ensure above, workshop organizers will submit a proposal to establish ICES-IOC study group on Nutrients Standard to IOC 25th general assembly, June 2009, and ICES annual meeting, September 2009 in appropriate time and manner in cooperation with IOC and ICES.

Participants have agreed to start more international co-operations discussed during the workshop. These action items are shown in separate page in this workshop report.

4. SUMMARY

The World's ocean is greatly impacted by the global environmental changes that are occurring due to the heat and gas exchange processes. Particularly, the fact that the ocean is absorbing the CO_2 in the atmosphere works effectively to slowdown global warming which is currently a potentially critical global problem.

Accordingly, it is a critical issue to determine the amount of anthropogenic CO_2 transported into the ocean interior more accurately, in order for studying and forecasting the global warming effects. However, because the global comparability of nutrients concentration data in the world ocean for calculating the human-induced CO_2 effects has not yet been established, it is still difficult to find out at this time whether the nutrients concentration changes in the ocean interior are natural fluctuations or are caused by human activities (Bindoff et al., 2007). This is essentially due to the lack of any global comparability of nutrients concentrations.

The requirement for the development of reference materials for nutrients in seawater, RMNS, in order to be able to accurately measure and compare nutrients in seawater, has been pointed out by the IOC and other organizations (IOC-IAEA-UNEP, 1995), and the research has also been continuing to be presumed. However, the desired RMNS has not yet been achieved.

In order to work towards improving the situation, the "2007 Workshop on chemical reference materials in ocean science" (Aoyama et al, 2008) was held in Tsukuba, Japan, in October 2007, at which meeting the international collaboration present agreed to begin the process to be able to establish a global comparability of nutrients concentration.

CRM's (Certified Reference Materials) for establishing the traceability of nutrients data are now under the ongoing process of certification for the RMNS, at the NMIJ (National Metrology Institute of Japan), and such CRMs for nutrients analyses are expected to be distributed sometime in the very near future.

Inter-laboratory comparison studies for RMNS were conducted in 2003 and 2006, and then followed again by an exercise performed by 58 laboratories from 15 countries in 2008, and the high level of internal comparability in each laboratory was indicated.

Some organizations have already performed the high accuracy observation of nutrients in seawater using the RMNS (Aoyama et al., 2006, 2007, 2008), and the effort to establish the comparability of nutrients data has been started. It was evaluated that we needed to hold an international workshop in order to be able to make progress with the discussions and agreements for such international activities.

For that reason, this workshop was held at UNESCO in Paris in February 2009, which had 40 researchers from two international organizations and 11 countries. At the meeting, following much discussion, the participants agreed to the following major decisions:

1) By establishing the INSS (International Nutrients Scale System), the comparability and traceability of nutrients data in seawater can be ensured. Thus, not only the study for nutrients in seawater itself will move forward, but also the amount of accumulated anthropogenic CO_2 will be accurately evaluated, as knowledge of both of these parameters are essential for the study for global warming.

2) By ensuring the comparability of pH measurements, the evaluation of the impact to the ocean of acidification, due to the increased amount of emissions of anthropogenic CO_2 to the atmosphere, will become possible.

3) By publishing a new manual for nutrients analysis, the analytical methods with the greatest accuracy which is currently being achieved by our community can be shared with the remainder of the world science community. These decisions are expected to contribute to the improvement of the studies of nutrients in seawater, as well as the study of both of global warming and ocean acidification, due to increased emission of anthropogenic CO_2.

5. ACTION ITEMS

1) A three-year international collaboration exercise for verifying the stability of RMNS will be conducted among the core 10 laboratories, 2 labs (JAMSTEC and SIO) from the Pacific side and 8 labs (Europe, USA, Canada) from the Atlantic side. A few lots of RMNSs will be measured by the participating laboratories precisely six times every six months from April 2009.

2) By conducting this exercise and ensuring that laboratories not currently within the programme join up, then the comparability of nutrients data across the world begin to be ensured for the future. Studies for the nutrients variability in the oceans, and estimations of accumulated anthropogenic CO_2 in the ocean interior will then start to be carried out more consistently.

3) To prepare for the international collaboration exercise for pH measurement reference materials, in order to make possible comparable direct measurements of ocean acidification. In this inter-laboratory comparison, we will use tris buffer and natural seawater preserved with HgCl2.

4) To accelerate the study for expanding the present RMNS to Ammonium and dissolved organic material (DOC, DON, DOP).

5) To complete the revised nutrients analysis manual before the end of October 2009. This will facilitate and improve the measurement accuracy of nutrients and ensure the data comparability as well.

6) To submit the draft plan for establishing INSS to ICES at the 25th IOC General Assembly to be held in June 2009 in order to establish the system which ensures the comparability and traceability of nutrients data continuously, by an internationally recognized working group. With this system, the comparability and traceability of nutrients data will be ensured into the future.

7) To make a proposal for reflecting the outcomes of this workshop to the GO-SHIP white paper.

8) To distribute 10,000 bottles of nutrients Standards to the key laboratories which take primary responsibility for maintaining the accuracy of nutrients measurement in the CLIVAR cruises, or the relevant countries, if the budget (scientific research fund has been applied) is guaranteed.

9) To conduct the proficiency test of RMNS with a new protocol in the near future. To carry out an RMNS inter-laboratory study in 2010 and 2012.

10) To carry out a comparison study of silicate stock solution among the 2008 RMNS I/C study laboratories, in order to examine relatively larger variability of silicate date reported by the participants. NIOZ will coordinate this silicate stock solution study.

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Annexes

Annex I

List of Participants

Dr. Marta Alvarez
IMEDEA
CSIC - Univ. Illes Balears
C/Miquel Marques 21, Esporles 07190
Spain
E-mail: marta.alvarez@uib.es

Ms. Carol Anstey
Ocean Research and Monitoring Section
Bedford Institute of Oceanography
1 Challenger Dr., Dartmouth, Nova Scotia,
B2Y 4A2
CANADA
E-mail: ansteyc@mar.dfo-mpo.gc.ca

Dr. Michio Aoyama
Geochemical Research Department
Meteorological Research Institute
1-1 Nagamine, Tsukuba, Ibaraki, 305-0052
JAPAN
E-mail: maoyama@mri-jma.go.jp

Mr. Karel Bakker
Marine Chemistry Department
Royal Netherlands Institute for Sea Research,
NIOZ
PO Box 59 1790 AB Den Burg
The Netherlands
E-mail: karelb@nioz.nl

Ms. Susan Becker
Scripps Institution of Oceanography
University of California, San Diego
UCSD9500 Gilman Drmc0214 San Diego
CA 92093
USA
E-mail: sbecker@ucsd.edu

Mr. Stephen Coverly
SEAL Analytical GmbH
Werkstrasse 4, 22844 Norderstedt
Germany
E-mail:stephen.coverly@seal-analytical.com

Dr. Anne Daniel
DYNECO/PELAGOS
Institut français de recherche pour l'exploitation de la mer
Technopole Brest Iroise BP 29280 Plouzané
France
E-mail: anne.daniel@ifremer.fr

Prof. Andrew Dickson
Scripps Institution of Oceanography
University of California, San Diego
9500 Gilman Drive, La Jolla, CA 92093-0244
USA
E-mail: adickson@ucsd.edu

Mr. Olivier Grosso
CNRS- Centre d'Océanographie de Marseille,
Laboratoire d'Océanographie Physique
et Biogéochimique
Campus de Luminy - Case 901, 163 avenue
de Luminy, 13288 Marseille Cedex9
France
E-mail: olivier.grosso@univmed.fr

Mr. Steven van Heuven
Department of Ocean Ecosystems
Groningen University
P.O.Box 14, 9750AA Haren,
The Netherlands
E-mail: svheuven@gmail.com

Dr. Maria Hood
International Ocean Carbon Coordination Project
IOC/UNESCO
1 rue Miollis 75732 Paris cedex 15
France
E-mail: m.hood@unesco.org

Dr. David J. Hydes
Natural Environment Research Council,
National Oceanography Centre
Southampton, SO14 3ZH,
UK
E-mail: djh@noc.soton.ac.uk

Ms. Dorete Weysmann Jensen
Marine Ecology,
National Environmental Research Institute
Aarhus University
Frederiksborgvej 399, DK- 4000 Roskilde
Denmark
E-mail: BLM@DMU.dk

Ms. Eileen Joyce
Marine Institute
Rinville, Oranmore, Co. Galway
Ireland
E-mail: eileen.joyce@marine.ie

Mr. Kazunobu Kawamoto
BL TECH
matsumoto-builingF4, 14-15
nihonbashiohdenmacyo
Chuo-ku, Tokyo, 103-0011
JAPAN
E-mail: Kawamoto@bl-tec.co.jp

Mr. Roger Kerouel
DYNECO/PELAGOS
Institut français de recherche pour l'exploitation de la mer
Technopole Brest Iroise BP 29280 Plouzané
France
E-mail: roger.kerouel@ifremer.fr

Ms. Rita Kramer
Section Nutrients
Bundesamt für Seeschifffahrt und Hydrographie,
Wüstland 2, 22589 Hamburg,
Germany
E-mail: rita.kramer@bsh.de

Ms. Berit Langkilde
Marine Ecology
National Environmental Research Institute,
Aarhus University
Frederiksborgvej 399, DK- 4000 Roskilde
Denmark
E-mail: dwj@dmu.dk

Dr. Kazuhiro Misumi
Environmental Science Research Lab,
Central Research Institute of Electric Power Industry
1646 Abiko, Abiko-shi, Chiba-ken, 270-1194
JAPAN
E-mail: misumi@criepi.denken.or.jp

Mr. Hitoshi Mitsuda
Laboratory for Instrumentation and Analysis
The General Environmental Technos Co., LTD
KANSO Technos
3-1-1 Higashikuraji, Katano, Osaka 576-0061
JAPAN
E-mail: mituda_hitosi@kanso.co.jp

Dr. Pascal Morin
Marine Chemistry Laboratory
CNRS & Univ. Pierre et Marie Curie Paris VI & Univ. Bretagne Occidentale
Observatoire Océanologique de Roscoff B.P. 74
Place Georges Teissier 29682 Roscoff cedex
France
E-mail: pmorin@sb-roscoff.fr

Ms. Asami Murao
Laboratory for Instrumentation and Analysis
The General Environmental Technos Co., LTD
KANSO Technos
3-1-1 Higashikuraji, Katano, Osaka 576-0061
JAPAN
E-mail: kanso_murao@kanso.co.jp

Dr. Akihiko Murata
Research Institute for Global Change
Japan Agency for Marine-Earth Science
and Technology
2-15 Natsushima, Yokosuka, Kanagawa.
237-0061
JAPAN
E-mail: murataa@jamstec.go.jp

Dr. Günther Nausch
Dept. Marine Chemistry
Leibniz Institute for Baltic Sea Research
Seestraße 15, D-18119 Rostock-Warnemünde
Germany
E-mail:guenther.nausch@io-warnemuende.de

Dr. Florence Nedelec
Laboratoire Environnement Ressources
de Normandie
Institut français de recherche pour
l'exploitation de la mer
Avenue du Gal de Gaulle, B.P.32,
14520 Port-en-Bessin
France
E-mail: F.Nedelec@ifremer.fr

Mr. Hidekazu Ota
The General Environmental Technos Co., LTD
KANSO Technos
Anwatukasa Bldg. 3F , 2-10
kandatukasamachi, Chiyodaku, Tokyo
101-0048
JAPAN
E-mail: ota_hidekazu@kanso.co.jp

Ms. Susan Reynolds
Scripps Institution of Oceanography
University of California San Diego
9500 Gilman Dr. 0214, San Diego, CA 92093
USA
E-mail: smreynol@ucsd.edu

Dr. Patrick Roose
Royal Belgian Institute for Natural Sciences
QUASIMEME, ICES
3e en 23e Linieregimentsplein, B-8400 Oostende,
BELGIUM
E-mail: patrick.roose@mumm.ac.be

Mr. Malcolm Rose
Marine Laboratory
Fisheries Research Services
FRS Marine Lab, 375 Victoria Road, Aberdeen,
AB11 9DB.
United Kingdom
E-mail: m.rose@marlab.ac.uk

Mr. Kenichiro Sato
Department of Marine Science
Marine Works Japan Ltd.
2-16-32 4F Kamariyahigashi,
Kanazawa-ku, Yokohama 236-0042
JAPAN
E-mail: satok@mwj.co.jp

Prof. Jonathan H. Sharp
College of Marine and Earth Studies
University of Delaware
700 Pilottown Road Lewes, DE 19958
USA
E-mail: jsharp@udel.edu

Dr. Toste Tanhua
Leibniz Institute of Marine Sciences
Marine Biogeochemistry
Duesternbrooker Weg 20 D-24105 Kiel,
Germany
E-mail: ttanhua@ifm-geomar.de

Ms. Evaline van Weerlee
Marine Chemistry Department
Royal Netherlands Institute for Sea Research,
NIOZ
Landsdiep 4 , 1797SZ, Den Hoorn
The Netherlands
E-mail: weerlee@nioz.nl

Dr. Sieglinde Weigelt-Krenz
Section Nutrients
Bundesamt für Seeschifffahrt und Hydrographie,
Wüstland 2, 22589 Hamburg
Germany
E-mail: sieglinde.weigelt@bsh.de

Dr. Malcolm Woodward
Plymouth Marine Laboratory
Prospect Place, Plymouth, PL1 3DH
UK
E-mail: EMSW@pml.ac.uk

Dr. Takeshi Yoshimura
Environmental Science Research Laboratory,
Central Research Institute of Electric Power Industry
1646 Abiko, Abiko-shi, Chiba-ken, 270-1194
JAPAN
E-mail: ytakeshi@criepi.denken.or.jp

Ms. Agnès Youenou
DYNECO/PELAGOS
Institut français de recherche pour l'exploitation de la mer
Technopole Brest Iroise BP 29280 Plouzané
France
E-mail: agnes.youenou@ifremer.fr

Dr. Jia-Zhong Zhang
Atlantic Oceanograpgic and Meteorological Laboratory,
National Oceanic and Atmospheric Administration
4301 Rickenbacker Causeway, Miami FL 33149
USA
E-mail: jia-zhong.zhang@noaa.gov

Staff for KANSO Technos
Ms. Yuko Nakamura
Kuno Ltd.
7-38-22-308, Higashi-Oizumi, Nerima,
Tokyo, 178-0063
JAPAN
E-mail: b8b84z@bma.biglobe.ne.jp

Staff for Workshop
Ms. Sachie Ishikawa
Geochemical Research Department
Meteorological Research Institute
1-1 Nagamine, Tsukuba, Ibaraki, 305-0052
JAPAN
E-mail: kagaku28@mri-jma.go.jp

Annex II

The Workshop Organizers

- Michio AOYAMA, Meteorological Research Institute, Japan
- Andrew DICKSON, University of California at San Diego, Scripps Institution of Oceanography, La Jolla, CA, USA
- David HYDES, National Oceanography Centre, Southampton, UK
- Akihiko MURATA, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan
- Jae OH, IAEA Marine Environment Laboratories, Monaco
- Patrick ROOSE, QUASIMEME, Wageningen, The Netherlands
- Malcolm WOODWARD, Plymouth Marine Laboratory, UK

Annex III

Workshop Agenda

February 10 (Tue.)

09:00~09:30	**Workshop Registration**

9:30~10:00	**OPENING SESSION** **Room 16**
	Welcome message
	Patricio Bernal (Executive Secretary of IOC/UNESCO)
	Message from sponsors
	Takeshi Yoshimura (CRIEPI)
	Anne Daniel (IFREMER)
	Patrick Roose (ICES)
	Opening massage from organizers
	Michio Aoyama (MRI)
	Maria Hood (IOC/UNESCO)

10:00~10:40	**Plenary talks**
	Chair person: Andrew Dickson **Room 16**
I-1	David Hydes and Michio Aoyama
	How do we improve the comparability of nutrients measurements?
P-1	J.v Ooyen, K. Bakker, E. Weerlee
	RMNS stability during Antarctic cruise

10:40~11:10	**Coffee**

11:10~12:30	**Plenary talks**
	Chair person: David Hydes **Room 16**
I-2	Kenichiro Sato and Michio Aoyama
	Comparability of Cruise-to-Cruise Using Reference Material for Nutrients in Seawater
P-6	Hidekazu Ota, Hitoshi Mitsuda , Munehito Kimura , Takashi Kitao, Yasuhiro Arii
	Development of RMNS (Reference Material for Nutrients in Seawater)
P-4	Anne Daniel
	Use of low-nutrients coastal water for national interlaboratory exercises

P-2	Michio Aoyama International Nutrients Scale System, INSS, in seawater, Proposal

12:30-14:00	**Lunch**

14:00-14:40	**Plenary talks** **Chair person: Malcolm Woodward Room 16**
P-5	Steven van Heuven The CARINA dataset effort
P-3	F. Nédélec, F. Bruchon, P. Riou, O. Pierre-Duplessix, V. Justome1, R. Le Goff, E. Rabiller Application of nutrients data for the eutrophication status assessment and management of coastal waters in Normandy (France) responding at the European Union Directives.

15:00-15:30	**Coffee**

14:40-16:20	**Poster** **Chair person: Akihiko Murata In front of Room 16**

16:20-17:50	**Plenary talks** **Chair person: Michio Aoyama Room 16**
I-5	Andrew Dickson Reference materials for seawater pH measurements
P-7	Akihiko Murata, Masao Ishii, Michio Aoyama, Hidekazu Ota, and Hitoshi Mitsuda Development of non-toxic RM for dissolved inorganic carbon
I-6	Jonathan Sharp DOC/DON Reference Material Use
P-8	Takeshi Yoshimura and Participants Reference Material of Nutrients in Seawater for dissolved organic phosphorus analysis

18:00-20:00	**Reception**

February 11 (Wed.)

09:00-10:40	**Plenary talks** **Chair person: Patrick Roose** **Room 16**
P-9	Stephen Coverly Quantifying, evaluating and recording instrument-and method-related performance parameters in a segmented-flow analyzer
P-10	Malcolm Woodward Ammonium analysis: search for the holy grail?
P-13	G. Nausch, M. Nausch, Ä. Welz, D. Setzkorn DOP measurements in the Baltic Sea - methodological aspects and results
P-14	Kazuhiro Misumi, Daisuke Tsumune, Takeshi Yoshimura, Yoshikatsu Yoshida, Frank O. Bryan, Keith Lindsay, Keith Moore, Scott C. Doney and Michio Aoyama Nutrients distributions simulated in an Ocean General Circulation model
I-4	Toste Tanhua Importance of accurate nutrients measurements for Cant inference

10:40-11:10	**Coffee**

11:10-12:10	**Sub group meetings** **Chair persons: Akihiko Murata, Takeshi Yoshimura, Malcolm Woodward**
	Room 16 RM of pH, non-toxic DIC RM **Room 16** Expand RM for DOC, DON and DOP references **Room 15** CFA technology

12:30-14:00	**Lunch**

11:50-12:30	**Sub group meetings continued** **Chair persons: David Hydes, Malcolm Woodward**
	Room 16 Nutrients manual update **Room 15** CFA technology

14:00-14:50	**Sub group meetings continued** **Chair persons: David Hydes**
	Room 16 Nutrients manual update

14:50-15:30	**Sub group meetings continued** **Chair persons: Michio Aoyama, Toste Tanhua**

Room 16 Short-term stability experiment -characterization of RMNS
Room 15 usage of nutrients data and carbonate system data in oceanography

15:30-16:00	**Coffee**

16:00-17:30	**Sub group meetings continued** **Chair persons: Michio Aoyama, Toste Tanhua**

Room 16 Short-term stability experiment -characterization of RMNS
Room 15 usage of nutrients data and carbonate system data in oceanography

Organizers meeting

19:00	**Workshop group dinner**

February 12 (Thu.)

09:00-10:30	**Reports of sub group meetings** **Chair person: Akihiko Murata Room 16**

10:30-11:00	**Coffee**

11:00-12:30	**Discussion on INSS** **Chair person: Michio Aoyama followed by lunch**

14:00-15:15	**General Discussion** **Chair person: Andrew Dickson Room 16**

15:15-15:45	**Coffee**

15:45-16:30	**Closing session** **Chair person: David Hydes Room 16**

Annex IV

List of Abbreviations

AAIII: Auto Analyzer III

AMT: Atlantic Meridional Transect

AOML: Atlantic Ocean Marine Laboratory

BEC: Biogeochemical Elemental Cycling

BIO: Bedford Institution of Oceanography

CARINA: Carbon in the North Atlantic

CCMA: Center for Coastal Monitoring and Assessment, NOAA

CFA: Continuous Flow Analysis

CFC's: Chlorofluorocarbons

CLIVAR: Climate Variability and Predictability

CRIEPI: Central Research Institute of Electric Power Industry, Japan

CRMs: Certified Reference Materials

CSK: Cooperative Survey of Kuroshio

DIC: Dissolved Inorganic Carbon

DOC: Dissolved organic carbon

DON: Dissolved organic nitrogen

DOP: Dissolved organic phosphate

EU: European Union

GESREM: Group of Experts on Standards and Reference Materials

GLODAP: Global Ocean Data Analysis Project

IAEA: International Atomic Energy Agency

ICES: International Council for the Exploration of the Sea

IFREMER: Institut francais de recherche pour l'exploitation de la muer, France

IMR: Institute of Marine Research, Helsinki

INSS: International Nutrients Scale System

IOC: Intergovernmental Oceanographic Commission

IOCCP: International Ocean Carbon Coordination Project

IPCC: Intergovernmental Panel on Climate Change

JAMSTEC: Japan Agency for Marine-Earth Science and Technology

JGOFS: Joint Global Ocean Flux Study

JPY: Japanese Yen

JRM: Japanese Reference Material

KANSO: General Environmental Technos Co., Ltd., Japan

LNSW: Low Nutrient Sea Water

MLRs: Multiple Linear Regression

MRI: Meteorological Research Institute, Japan

MUMM: Management Unit of the North Sea Mathematical Models

NCAR: National Center for Atmospheric Research

NIOZ: Royal Netherlands Institute for Sea Research

NMIJ: National Metrology Institute of Japan

NOAA: National Oceanic and Atmospheric Administration, USA

NOC: Natural Oceanography Centre

NRC: National Research Council of Canada

NSF: U.S. National Science Foundation

NSOPs: Standard Operating Procedures (SOPs) for the nutrients measurements

NUTS I/C 4: 4th Nutrients In the Comparison

OSI: Ocean Scientific International

PIs: Principal Investigator

PML: Plymouth Marine Laboratory

QC: Quality Control

QUASIMEME: Quality Assurance of Information for Marine Environmental Monitoring in Europe

RMNS: Reference Materials for Nutrients in Seawater

SCOR: Scientific Committee on Oceanic Research

SEAL analytical:

SFA: Segmented Flow Analyser

SGONS: The Joint ICES-IOC Study Group on Nutrients Standards

SOPs: Standard Operating Procedures

TA: Total Alkalinity

TDN: Total Dissolved Nitrogen

TDP: Total Dissolved Phosphate

TN: Total Nitrogen

TP: Total Phosphate

UNEP: United Nations Environmental Programme

UNESCO: United Nations Educational Science and Culture Organization

WHPPC: WOCE Hydrographic Programme Committee

WOCE: World Ocean Circulation Experiment