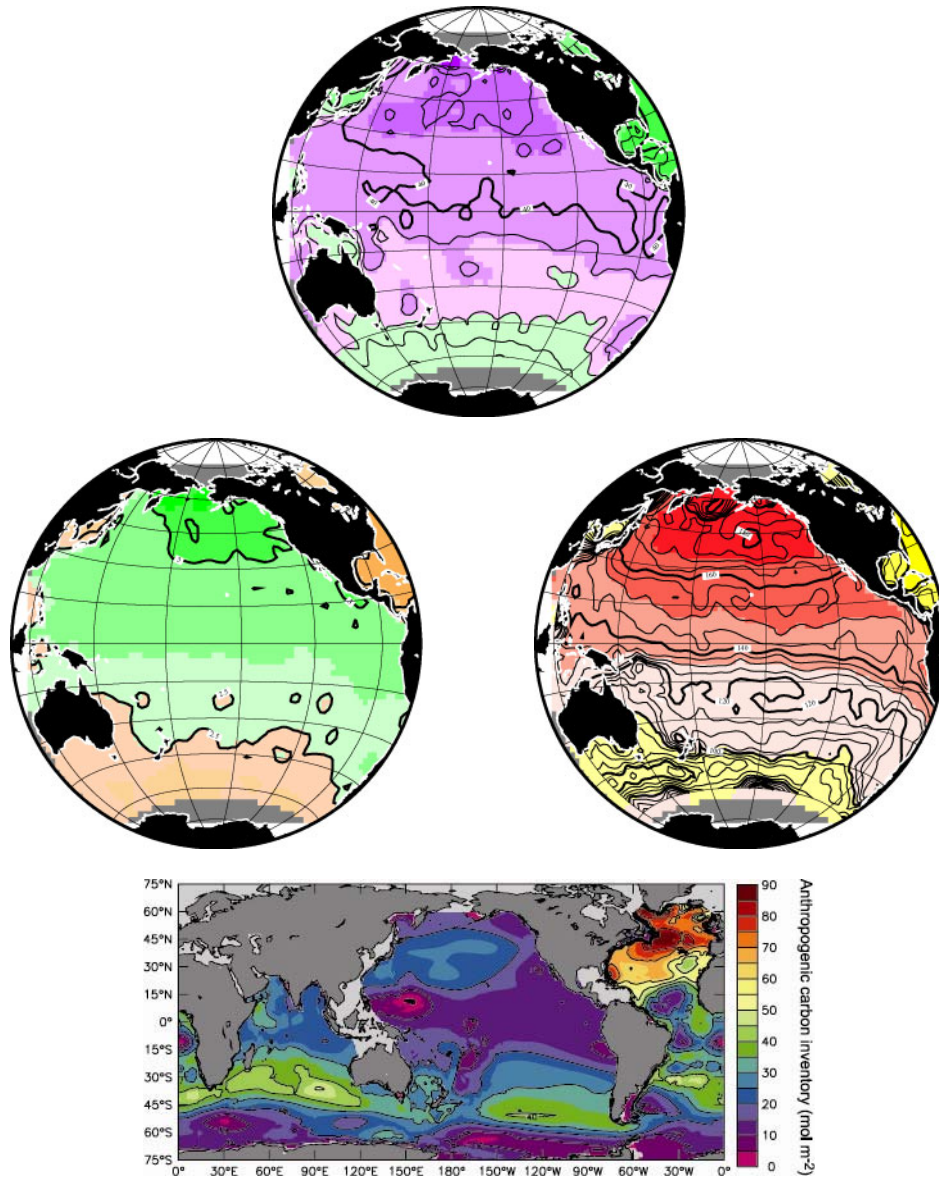


Draft

*2007 Workshop on Chemical Reference
Materials in Ocean Science, WCRMOS, report*



29 October — 1 November 2007

Tsukuba International Congress Center --EPOCHAL

Tsukuba, Japan

The upper three figures are Nitrate (top), Phosphate (left) and Silicate (right) distribution in the Pacific Ocean at 2000m depth. These figures are produced by M. Aoyama basing on WOA05 database.

The bottom figure is Figure 5-10 of the following article.

Bindoff, N.L., J. Willebrand, V. Artale, A. Cazenave, J. Gregory, S. Gulev, K. Hanawa, C. Le Quéré, S. Levitus, Y. Nojiri, C.K. Shum, L.D. Talley and A. Unnikrishnan, 2007: Observations: Oceanic Climate Change and Sea Level. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Figure 5.10. Column inventory of anthropogenic carbon (mol m^{-2}) as of 1994 from Sabine et al. (2004b). Anthropogenic carbon is estimated indirectly by correcting the measured DIC for the contributions of organic matter decomposition and dissolution of carbonate minerals, and taking into account the DIC concentration the water had in the pre-industrial ocean when it was last in contact with the atmosphere. The global inventory of anthropogenic carbon taken up by the ocean between 1750 and 1994 is estimated to be $118 \pm 19 \text{ GtC}$

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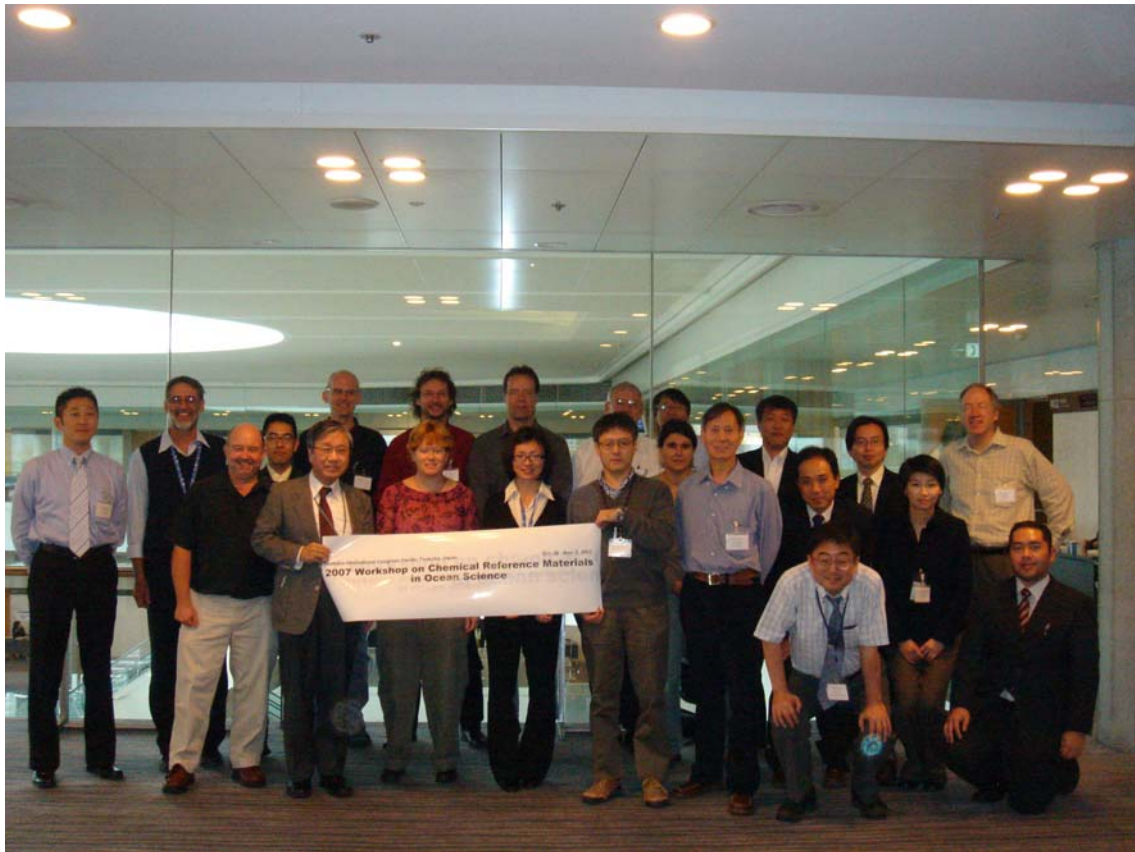
SUMMARY REPORT

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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 particularly for studies of global change. With global climate changes there is the requirement for better comparability between data sets so as it is possible to investigate reliably the tight coupling between the nitrogen and phosphorus cycles in the ocean, with that of carbon. 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 CO₂ parameters, and the current status of available chemical reference materials, particularly for nutrient 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 nutrient data. The agreements at this workshop in Tsukuba 2007 marked an epoch in the history of nutrient comparability.

In this report, the details of the presentations and discussions in the workshop are summarized.

2. OBJECTIVES OF THE MEETING

- 1) Review the current status of available chemical reference materials in ocean science
- 2) Establish international collaborations to promote the use and development of chemical reference materials in ocean science
- 3) Discuss the future tasks on the use/development of chemical reference materials
- 4) Discuss a proposed “International Nutrients Scale System” to establish comparability of nutrients data in the world ocean

3. SESSIONS OF THE MEETING

Session 1: Reviewing the current status and availability of chemical reference materials in ocean science

Session 2: Towards establishing international collaborations in the use and development of chemical reference materials in ocean science

Session 3: Comparability and traceability of ocean CO₂ measurements

Session 4: Results of 2006 RMNS intercomparison

Session 5: “International Nutrients Scale System” to establish comparability of nutrients data in the world ocean

Session 6: Discuss the future tasks on the use/development of chemical reference materials in ocean science

Session 7: General discussion

4, SESSION SUMMARIES

Session 1: Reviewing the current status and availability of chemical reference materials in ocean science.

Co-chair: David J. Hydes & Jae Ryoung Oh & Akihiko Murata

The QUASIMEME proficiency testing scheme: history, results and future trends of the nutrient programme.

Patrick Roose¹, Steven Crum² and Wim Cofino²

Between 1993 and 1995 the European Union (EU) supported the Quasimeme project which had the aim to develop a holistic quality assurance program for marine environmental monitoring information in Europe. The EU funded Quasimeme project demonstrated that laboratories which followed on a regular basis the learning programs and the laboratory testing schemes improved the quality of their data.

Since 1996 the subscription scheme has included the matrix-determinant combinations relevant for national and international marine QA programmes. These were typically heavy metals in sediment and biota, polychlorinated biphenyls in sediment and biota and, nutrients in seawater.

The nutrient part of the project has the longest history starting in 1991. Over the years on average about 65 laboratories from about 55 countries participated in the scheme. In general more than 70% of the laboratories have for >75% their values a z-score that is <|2|. A clear improvement can be seen for those labs that have continuously been part of the programme. performance. The interlaboratory variability or coefficient of variation is generally less than 10% for most nutrients, with the exception of ammonia.

The recently adopted water framework directive will require member states to monitor nutrients in their surface waters which include coastal and transitional waters that are already part of QUASIMEME.

Interlaboratory Comparison for the Yellow Sea Large Marine Ecosystem

Dan Wruck

In the approved Implementation Plan of the UNDP/GEF Yellow Sea Project, “Reducing Environmental Stress in the Yellow Sea Large Marine Ecosystem”, one of the activities of the Pollution Component was a regional inter-calibration exercise between selected laboratories from China and Korea. The parameters for inter-calibration were nitrite, nitrate, phosphate (dissolved) and silicates.

Applicants who returned results from the first interlaboratory trial conducted in January 2006 were eligible to participate in the second round testing undertaken in August 2006.

Queensland Health Scientific Services (QHSS) undertook the exercise. QHSS is internationally accredited to ILAC Guide 13 for conducting proficiency testing programs.

All the samples supplied were natural saline water samples representative of the range of sample types commonly encountered for nutrient measurement. All of the samples supplied had previously been used in a large collaborative trial program and each of the samples and parameters being evaluated had been characterized as Certified Reference Materials.

All participants were supplied a detailed questionnaire which requested details on the methodology and the instrumentation type from each of the participating laboratories. All of the data was compared and evaluated against their respective certified values.

In general, the median results were close to or within the certified range for both the interlaboratory exercises. Overall, the analysis of ammonium and silica improved from the first exercise, while the quality of the phosphorus and nitrogen oxides was not so good. Not all laboratories supplied data for ammonium, even though it is a priority nutrient. Most laboratories used similar chemical methods for the analyses; however there was a range of instrumental types used in the measurements.

“Experience on reference material from ICES intercomparison exercises” by Anne Daniel, Alain Aminot, Roger K erouel, presented by Anne Daniel, IFREMER, France

In the 1990s a number of studies were organized under the ICES umbrella. These studies have been well documented (see Aminot & Kirkwood ,1995). In Europe these helped lead into the setting up of QUASIMEME (described in the earlier talk by Patrick Roose) which is now world wide programme. Historically, the only way to determine the comparability of nutrient analyses performed by different laboratories has been by conducting inter-laboratory comparison experiments. These have provided consensus values plus uncertainties for nutrient concentrations reported by the different laboratories. The ICES Nutrient Inter-comparisons were carried out five times from 1965 (Aminot and Kirkwood, 1995).

Following ICES 4 Ifremer offered to check whether reference samples could be obtained by spiking low nutrient natural seawater. Ifremer found that spiked low nutrient natural seawaters were unstable due to poorly controlled biological activity. Only very low nutrient concentrations remained unchanged and could be used to control nutrient analytical blanks. Ifremer concluded that only sterile water could be expected to maintain its nutrient concentrations unchanged at any level. Reliable sterilisation could be provided by autoclaving (120  C, 20 min), and then no subsequent transfer of treated water until the water was analysed. Individual samples bottles had to be tightly closed before the treatment, then opened only for analysis. Autoclaving proved to be a potentially reliable method to preserve nutrient species in seawater reference material (Aminot &K erouel., 1991; 1995). Autoclaving was used for subsequent intercomparison exercises [NUTS I/C5 (Aminot & Kirkwood. 1995), French exercises, and for the QUASIMEME Programme].

Autoclaving has drawbacks. Plastic bottles are damaged at the temperatures and pressures used. Silicate has to be excluded due to contamination as glass bottles have to be used. Phosphate species may precipitate (samples have to be acidified to pH = 7 before treatment to prevent this). Critically for the production of large numbers of samples a voluminous and expensive autoclave would be required.

Due to these problems with autoclaving Ifremer has tested the effectiveness of pasteurisation. For this samples are held at about 80 C, for a few hours. This has found to be equally effective as autoclaving but with some advantages (Aminot & K erouel, 1997; 1998). The advantages are that plastic bottles can be used so that silicate can be included, phosphate is less liable to precipitate, ammonia is stable for at least 6 months and normally available laboratory ovens can be used. This method is currently being

used by Ifremer to prepare samples for French intercomparison exercises.

Conclusions

We are now aware of the many problems surrounding the preparation of adequately stable reference material for nutrients. This awareness has now lead to an understanding of how to over come the problems. We feel that satisfactory reference materials can be prepared. We feel also that a single material will not cover all needs. Specific materials are required for different applications.

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“The Development of Reference Material for Nutrients in Seawater in a Seawater Matrix” by Hidekazu Ota, Yasuhiro Arii, Munehito Kimura Takashi Kito, presented by Hidekazu Ota

The importance of developing RMNS has been recognize international for a number of

years for example IOC – IAEA – UNEP recommended the development of RM during the workshop in 1991-1993; and the National Academies in the US clearly stated the need for an RMNS in 2001. Effective RMNS materials are needed not only for long-term monitoring of nutrients in the ocean sciences, but in the study of climate change. For WOCE, the required accuracy was better than 1%, and the repeatability (precision) was 0.2%, but to achieve this degree of precision in inter-comparability in future between laboratories analysis of the WOCE data has shown that RMNS materials are needed.

The major objective in making a RMNS is to establish traceability and comparability of nutrient data in seawater in the world ocean. The objectives were to produce RMNS solutions that were:- homogeneous across a lot; stable for several years; based on 100% natural sea water without the use of toxic preservatives; available at a range multiple concentration to covers different ocean condition and also to help detect non-linear calibrations. In addition all the nutrients of interest should be present in each solution. It was thought that batches of 2000 of bottles per lot were needed to support global projects. The material should be stable at room temperature.

The final aim was to have the material linked to the International System of Units (abbreviated SI from the [French](#) *Le Système international d'unités*) by collaboration with a standards institute to provide a recognized certification (see talk by Hioki).

To prepare RMNS material to strict standards The General Environmental Technos Co., Ltd. has built a “factory”. The RMNS is made using a natural seawater base with salinity of about 35. The concentrations of RMNS for nitrate, nitrite, silicate and phosphate can range from very low - nearly zero, to higher concentrations observed in the mid depth of the Pacific Ocean. To achieve this waters are mixed from different sources. The water with the appropriate concentrations is autoclaved in a 230 litre stainless steel autoclave. (Tests have been carried out to find the most suitable vessel). After the water has cooled it is stirred and bottled in a clean room, under “class 100” conditions. An automated bottling machine is used. Plastic bottles are used which have been washed in high purity water and UV light sterilised by the manufacturer. Each batch takes about 2 weeks to prepare. There are 20 users of these solutions in Japan at the moment (early 2007). These solutions were used for the 2006 intercomparison organized by Michio Aoyama.

The stability and homogeneity of RMNS solution produced by this “factory” have now been checked over a period of four years.

The table compares results from (1) “MIRAI”: measurements by JAMSTEC/MWJ, On board R V MIRAI (2) “2006 IC”: 2006 Intercomparison Exercise (3) “KT” :Factory measurement data from the date of production to the most recent measurement. .

LotNo. Production date	ANAL. Lab.	$\mu\text{mol/kg}$		
		N itrate	Phosphate	S ilicate
BA 2005.JAN06	M R I	0.1 ± 0.0	0.10 ± 0.01	1.6 ± 0.1
	2006C	0.1 ± 0.0	0.00 ± 0.00	1.7 ± 0.2
	KT	0.1 ± 0.1	0.05 ± 0.02	1.6 ± 0.3
AY 2004.O CT21	M R I	5.6 ± 0.0	0.52 ± 0.01	30.1 ± 0.1
	2006C	5.7 ± 0.2	0.49 ± 0.03	30.2 ± 1.1
	KT	5.6 ± 0.3	0.50 ± 0.01	29.7 ± 0.4
AX 2004.O CT20	M R I	21.4 ± 0.1	1.61 ± 0.01	59.5 ± 0.1
	2006C	21.6 ± 0.4	1.59 ± 0.04	58.9 ± 0.9
	KT	21.4 ± 0.2	1.58 ± 0.01	58.9 ± 0.5
AV 2004.FEB15	M R I	33.4 ± 0.1	2.52 ± 0.01	157.9 ± 0.2
	2006C	33.6 ± 0.4	2.52 ± 0.04	155.8 ± 2.2
	KT	33.3 ± 0.1	2.49 ± 0.01	156.9 ± 1.0
AZ 2005.JAN05	M R I	42.3 ± 0.1	3.02 ± 0.01	137.2 ± 0.2
	2006C	42.4 ± 0.7	3.03 ± 0.04	135.4 ± 1.6
	KT	42.2 ± 0.2	2.98 ± 0.02	135.9 ± 0.4

“NMIJ’s (National Metrology Institute of Japan) plan of developing seawater CRMs on nutrients” by Akiharu Hioki, presented by Akiharu Hioki.

NMIJ is working with the RMNS community in Japan to develop a certification of the KANSO RMNS solutions by the end of 2008. (NMIJ had planned to develop CRMs for nutrients seawater based on NMIJ’s research history into nutrient salts.)

NMIJ will provide the necessary metrological traceability. This will be linked internationally through the CCQM (Comité Consultatif pour la Quantité de Matière métrologie en chimie). So far NMIJ has developed primary methods for nitrate and nitrite, phosphate and ammonium based on gravimetric analysis and coulometric titration. A method for silicate is still being developed. CCQM has started to look at the international comparison of calibration solutions for seawater analysis (<http://www.bipm.org/> CCQM-K59/P89 (2007) in which NMIJ participated

NMIJ’s plan is to develop a parallel range of analytical methods for the determination of nutrients in a seawater matrix. These will include work on colorimetry, ion chromatography and IEC-ICPMS as well as the improvement of primary standard solutions. In the table below NMIJ’s aims for providing comparative analysis of seawater solution by different methods is compared to what the marine science community would like to achieve and thinks it is presently capable of achieving.

Some of the presentations at the workshop are not included in this workshop report.

Session 2: Towards establishing international collaborations in the use and development of chemical reference materials in ocean science.

Co-chair: Patrick Roose & Katsumi Hirose

Summary of session 2 is not available in this version.

Session 3: Comparability of ocean CO₂ measurements.

Co-chair: Andrew Dickson & Hisayuki Inoue-Yoshikawa

Summary of session 3 is not available in this version.

Session 4: Results of 2006 RMNS inter-comparison

Co-chair: Akihiko Murata & David J. Hydes

Summary of session 4 is not available in this version.

- Session 5: “International Nutrients Scale System” to establish comparability of nutrients data in the world ocean.
Co-chair: Andrew Dickson & Patrick Roose
- Session 6: Discuss the future tasks on the use/development of chemical reference material in ocean science
Co-chair: Andrew Dickson & Patrick Roose
- Session 7: General discussion
Chair: Michio Aoyama

Session summaries of 5, 6 and 7 are presented together because the discussions showed tightly related each other.

Discussion on our large tasks:

Participants discussed on the tasks to establish global comparability of nutrients data in seawater. Dr. Dickson pointed out that we need to identify/clarify our large tasks as follows;

1. Goal: To provide mechanisms which nutrient data can be harmonized.
Made consistent results between lab/lab, place and time..
2. Ideal mechanisms proposed require continuity of particular project.
If scale is “destroyed”, can it be replaced? Goal: not necessary immediate
3. On production and distribution of RM, we need to put priority:
 - stable sample
 - set different sample, different level
 - we know that values, stability, well enough that can be used to calibrate. Those should be internally consistent.
 - Ideally we would obtain “right” answer.

Discussion on certification of RM:

On the certification of the RM, Karrel pointed that certification would be based on the inter-comparison study. Dan also pointed the difficulty of certification of RM and in the process of the certification it should be used at least two methods of the measurements.

Uncertainty would be also one of the difficulties when certify RM. We also need to know “how to use RM”. There is less evidence of the stability of RM at this moment and a question is that what kind of evidence of stability we need?

We also need to feel confident in a strategy to produce a “nutrient-free” seawater. Need to choose a desired level of stability. Need to agree on an approach to validate the stability of the proposed RM.

Target CRM uncertainty would be 1%, therefore, stability of CRM should be 0.5%.

Stability: <0.5% of deep Atlantic level over 3 years

A poisoned stock solution + nutrient free sea water is a way to keep comparability.

What nutrients to measure? (Si, P, NO₃, (NO₂, NH₃))

Do we expect stability in all? Or few? Need to check for all or none

How much do we need to validate RM?

One use their own way of concentration and preparation when they use the low nutrients seawater during the measurements.

Degree of Verification:

Characterization of material, RM, would be done by group of “core” laboratories. Each core laboratory should be measure RM by same method during the periods of characterization. We also need data center to collect the results in each laboratory and feedback the results to all core laboratories.

Discussion on how to use RM after we have confidence about nutrients concentrations of RM.

There are three ways to use RM.

1. As Quality Assurance sample which is measured with target samples.
2. As Calibration. We need to check stability first before we use RM as calibration standard.
3. To correct data as Fixed point, this way is similar with NIOZ tracking tracer.

We can not do these three ways using one batch of RM. If we have appropriate two batches of RM, we can do 1 and 3 among three ways above. The ways of use RM depend on costs.

How many concentration levels of RM do we need?

We need to consider matrix differences between Pacific seawater and Atlantic seawater. We need a level at 2/3 of full concentration of calibration standards.

We need to provide Atlantic seawater to KANSO. The amount of seawater per lot is about 250- 300 liter. Aoyama asked to do pasteurization onboard just after collected to stop biological activity in collected seawater during transport.

2 levels each of 1/3 and 2/3 of full scale might be prepared, this means that total number would be 4 batches.

Discussion on characterization of RM:

After we prepare these batches, we can start to confirm stability and to work towards assigned value, and characterize the RM.

Who contribute stability test? At the laboratories doing stability test, same LNS should be used when preparing standard cocktail. We need two cocktail mix for Pacific and Atlantic. NIOZ would take this part.

How frequent do we compare cocktail and RM?

Monthly, quarterly, every half year and yearly bases depend on the availability in each laboratory.

We assign core laboratories as below where frequent measurement is requested.

PML (UK)

MUMM(Be)

IFREMER(Fr)

NIOZ(NI)

JAMSTEC, NOC, SIO would also participate this stability test, but not so frequent measurements would be done. QUASIMEME has potential to serve as central data center of stability test.

Laboratories would report the concentrations of LNSW Blank, cocktail and RM.

Do we assign value of RM? We can use accumulated data as "real" data.

KANSO also do stability test accordance with Guide 34, 35.

Assignment of Values would be done based on results from runs for stability test. We also need report of uncertainty. INSS need "assigned" value. We do stability test for three years and prepare report of stability test to tell the community. We also need to update analytical method of nutrients in seawater.

In three years, results of stability test of RM and obtained consensus concentration of RM together with certification of RM by metrological board, we have International Nutrients Scale System in seawater.

5. CONCLUSIONS

Workshop participants agreed to continue the international collaborations with the aim of establishing global comparability of the nutrients data from the world ocean.

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 will be held to discuss progress since 2007, and discuss future tasks.

6. Background of problem

The comparability and traceability of nutrients data in the world's oceans are fundamental issues in marine science, and particularly for studies of global change. Our community has been continuing to improve comparability of the nutrients data in the world ocean in many ways, including international inter-comparison experiments and also development of nutrients reference materials. 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 the nutrients comparability:

"Using the same data set extended to the world, large regional changes in nutrient ratios were observed (Li and Peng, 2002) but no consistent basin-scale patterns. Uncertainties in deep ocean nutrient observations may be responsible for the lack of coherence in the nutrient changes. Sources of inaccuracy include the limited number of observations and the lack of compatibility between measurements from different laboratories at different times (Bindoff et al., 2007)".

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 of certified reference seawater which can cover several determinants all in one bottle.

During the WOCE periods, WHPPC recognized the importance of comparability of WOCE nutrients data world wide. They recommended to all WOCE cruise PIs to participant ICES 6th inter-comparison (WOCE WHPPC, 199x), however, it could not done because ICES 6th inter-comparison was canceled.

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 lead 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 day to day 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, USA and the National Research Council of Canada (NOAA/NRC) had conducted two inter-comparison exercises to certify MOSS-1 (Willie and Clancy, 2000; Clancy and Willie, 2003). However, despite individual efforts, adequate comparability and traceability of nutrient 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, Japan, organized an inter-comparison study which include 18 laboratories (Aoyama, 2006, Aoyama et. al, 2007). In 2006 Michio Aoyama, of the Meteorological Research Institute, Japan working with Hidekazu Ota, of the General Environmental Technos Co., Ltd. (KANSO) organized second inter-comparison study which included 55 different laboratories world wide (Aoyama, 2007 in preparation). Both inter-comparison studies clearly show that global use of reference materials of nutrients in seawater would greatly improve the comparability of nutrients data in the world's oceans.

In early 2007 Michio Aoyama had visited NOC in Southampton. One of the reasons for their visit was to discuss the results of the inter-calibration. This was extended to an invitation to the European participants in the inter-calibration and other interested nutrient chemists 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 CO₂ parameters, and the current status of available chemical reference materials, particularly for nutrient 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 nutrient data. The agreements at this workshop in Tsukuba 2007 marked an epoch in the history of nutrient comparability.

7. Basic requirements of RM and status of present RM

7-1. Basic requirements of RM

The consensus of the world ocean chemists is that Reference Materials were needed and that these should: -

- (A) be available in sufficiently large batch sizes to be "internationally certifiable"
- (B) be available in sufficient quantities and at low enough price to encourage the extensive take up of these materials
- (C) have sufficiently long shelf life (3+ years) to allow comparison between cruises that may be few years apart.
- (D) be available in range of concentrations to cover the ranges of concentration needed in shelf sea, Atlantic Ocean and Pacific Ocean work.
- (E) be based on a "real seawater" - a salinity of 35 was considered to be the most appropriate matrix.
- (F) have a homogeneity of 0.1% or better.

It was thought that 6 solutions with the approximate concentrations listed below would be sufficient to cover the requirements of most oceanographic work from shelf seas to the north Pacific. This would allow workers to use 3 solutions to span the range of samples they would be processing

	Nitrate	Phosphate	Silicate
1	~0	~0	~0
2	5	.5	3
3	10	1	6
4	20	1.5	60
5	30	2.5	135
6	40	3.0	200

7-2. Status of present RM

Producing RMNS at KANSO

Seawater with various nutrient concentrations was collected from surface to deep waters in the western North Pacific Ocean. RMNS of specific concentrations of nutrients (one batch) was prepared as follows:

The seawater was gravity filtered with a membrane filter of 0.45- μ m pore size. A stainless steel container of 40-l to 200-l were used. The seawater was sterilized by autoclaving at 120 °C for 2 h; then the autoclaving were repeated twice. The autoclaving was based on previous studies (Aminot, 1991, 1995). After cooling for a few days to room temperature, an aliquot (90 ml) of autoclaved seawater in the stainless

steel container was filtered through a 0.22- μm pore size membrane into polypropylene (PP) bottles of 100-ml volume. These bottles had been rinsed by pure water and exposed to UV-light before they were used. To prevent subsequent contamination from air, and evaporation or condensation of water, each PP bottle was vacuum sealed in a vinyl bag. The bottling process was conducted throughout in a clean room class 1000¹⁴.

Homogeneity of present RMs

The homogeneities of the samples were measured separately. The homogeneities for 30 bottles of sample 2 of 2006 MRI intercomparison study are listed in table 1. Analytical precision was also estimated for 30 samples of natural seawater whose nutrient concentrations were similar to those of sample 3.

Table 1 Homogeneity of sample 2 of 2006 MRI intercomparison study and analytical precision

	Nitrate + nitrite	Phosphate	Silicic acid
Homogeneity of sample 2 (%)	0.22	0.32	0.19
Analytical precision (CV %)	0.22	0.22	0.12
Homogeneity of sample 3 (%) of 2003 intercomparison exercise	0.44	0.80	0.15

Note: The concentrations of nutrients in natural seawater for the simultaneous analyses were 43 $\mu\text{mol kg}^{-1}$ for nitrate + nitrite, 3.1 $\mu\text{mol kg}^{-1}$ for phosphate, and 148 $\mu\text{mol kg}^{-1}$ for silicic acid.

Long-term storage experiment had demonstrated that homogeneity and concentrations of nutrients were maintained about at room temperature for about 4 years and the detail of the long-term storage experiment is given elsewhere.

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ANNEXES I History of nutrient intercomparisons

This history of nutrient intercomparisons 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, which includes histories of the first to fourth ICES exercises. Histories of the fifth ICES exercise, the first and second NOAA/NRC intercomparisons, MRI 2003 and 2006 intercomparisons are also summarized in this appendix.

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:

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

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

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

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

Research vessels delivered bulk samples, which were subsampled 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 intercomparison 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!

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 Nutrient Methods²", 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.

4. Fourth ICES Exercise

Various "workshop" and multiship events following the ICES/SCOR exercise included nutrient 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.

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-nutrient natural seawater was spiked with known concentrations of nutrient 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 $\mu\text{mol L}^{-1}$ for nitrate and 0.08–1.85 $\mu\text{mol L}^{-1}$ for phosphate.

6. 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.

7. 2002 NOAA/NRC Intercomparison

An 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 suggest that the homogeneity problem identified in the first NOAA/NRC intercomparison exercise was overcome, although the orthophosphate data indicate a larger interlaboratory 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 $<\pm 10\%$ from the assigned mean. All laboratories used methodology based on colorimetric principles.

8. 2003 MRI Intercomparison

Autoclaved natural seawater was prepared for intercomparison samples. Sample homogeneity was confirmed by repeatability of measurement. Sets of 6 samples covering a concentration range greater than that in previous intercomparisons were distributed. The concentrations were 0–38 $\mu\text{mol kg}^{-1}$ for nitrate, 0–0.9 $\mu\text{mol kg}^{-1}$ for nitrite, 0–2.7 $\mu\text{mol kg}^{-1}$ for phosphate, and 0–136 $\mu\text{mol kg}^{-1}$ for silicic acid. 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 silicic acid,

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 interlaboratory discrepancy. Therefore use of a certified RMNS is essential for establishing nutrient data sets that can be compared across laboratories, especially for silicic acid and phosphate.

9. 2006 MRI Intercomparison

Autoclaved natural seawater was used for an interlaboratory comparison exercise for a reference material for nutrients in seawater in 2006 as well as a 2003 intercomparison exercise. Sample homogeneity was confirmed by repeatability of measurement and those for nitrate, phosphate and silicic acid were 0.2%, 0.3% and 0.2%, respectively. Sets of 6 samples covering a concentration range of 0.1–42.4 $\mu\text{mol kg}^{-1}$ for nitrate, 0.0–0.6 $\mu\text{mol kg}^{-1}$ for nitrite, 0.0–3.0 $\mu\text{mol kg}^{-1}$ for phosphate, and 1.7–156.1 $\mu\text{mol kg}^{-1}$ for silicic acid. A total of 55 sets of samples were distributed to 55 laboratories in 20 countries. Results were returned by 52 laboratories in 19 countries.

ANNEXES II Current available CRMs of Nutrients

List of CRMs currently available and its use.

Moos-1 (Canada) Ifremer, U. Plymouth Limited supply, expires in Dec. 2007
NLLNCT(Australia) Australia, KORDI
Sagami (CSK-Japan) in NaCl solution
VK1 (Eurofins-Denmark) Recently became certified (2006)
Future CRM by NMIJ/KANSO (Japan)

ANNEXES **III**

WORKSHOP PROGRAMME

WORKSHOP PROGRAMME

October 29 (Mon.)

09:30~10:00 **Workshop Registration**

10:00~10:20 **OPENING SESSION**

10:00~10:10 **Michio Aoyama**

Opening Remarks

10:10~10:20 **Katsumi Hirose**

Welcome speech

10:20~12:40 **SESSION 1 -- Reviewing the current status and availability of chemical reference materials in ocean science**

Co-chair: David J. Hydes & Jae Ryoung Oh

10:20~10:40 **Patrick Roose**

1-1 The QUASIMEME proficiency testing scheme: history, results and future trends of the nutrient programme

10:40~11:00 **Dan Wruck**

1-2 Interlaboratory Comparison for the Yellow Sea Large Marine Ecosystem

11:00~11:20 COFFEE

11:20~11:40 **Anne Daniel**

1-3 Experience on reference material from ICES intercomparison exercises

11:40~12:00 **Hidekazu Ota**

1-4 The Development of Reference Material for Nutrients in Seawater in a Seawater Matrix

12:00~12:20 **Akira Hioki**

1-5 NMIJ's plan of developing seawater CRMs on nutrients

12:20~12:50 DISCUSSION

12:50~14:00 LUNCH

14:00~15:30 **SESSION 1 -- Reviewing the current status and availability of chemical reference materials in ocean science (Continued)** Co-chair: Jae Ryoung Oh & Akihiko Murata

14:00~14:30 **Takashi Arai**

1-6 Accreditation for (C) RMP and Database of (C) RM

14:30~14:50 **Susan Beckere**

1-7 ODF/Chemistry Laboratory

14:50~15:10 **Kenichiro Sato**

1-8 Establishment of comparability of nutrients data obtained in R/V Mirai cruises based on Reference Material for Nutrients in Seawater (RMNS)

15:10~15:30 DISCUSSION

15:30~15:50 COFFEE

15:50~17:20 **SESSION 3 -- Comparability and traceability of ocean CO₂ measurements**
Co-chair: Andrew Dickson & Hisayuki Inoue-Yoshikawa

15:50~16:20 **Andrew Dickson**

3-1 Oceanic CO₂ reference materials: assigning uncertainty

16:20~16:50 **Akihiko Murata**

3-2 Development of nontoxic RM for dissolved inorganic carbon

16:50~17:20 DISCUSSION

19:00~21:00 (BERM11 reception, optional)

October 30 (Tue.)

11th International symposium on Biological and Environmental Reference Materials (BERM11) SESSION

The program is available at
<http://www.nmij.jp/berm11/Oct30-e.html>

19:15~21:40 Workshop Banquet (JPY5000)

October 31 (Wed.)

Workshop sub group meeting (Nutrients, INSS, carbonate system)

November 1 (Thu.)

09:00~10:20 SESSION 2 -- Towards establishing international collaborations in the use and development of chemical reference materials in ocean science

Co-chair: Patrick Roose & Katsumi Hirose

09:00~09:20 Jia-Zhong Zhang

2-1 An urgent need for nutrient standards in seawater

09:20~09:40 Hajime Obata

2-2 Intercalibration on GEOTRACES

09:40~10:00 Jae Ryoung Oh

2-3 History of IAEA-IOC-UNEP

10:00~10:20 Malcolm Woodward

2-4 Calibration of open ocean nanomolar nutrients

10:20~10:40 COFFEE

10:40~12:10 SESSION 4 -- Results of 2006 RMNS intercomparison

&

SESSION 5 -- "International Nutrients Scale System" to establish comparability of nutrients data in the world ocean

Co-chair: Akihiko Murata & David J. Hydes

10:40~11:00 Michio Aoyama

Recent Comparability of the Nutrients Data in the World Ocean: Results of 2003 and 2006 RMNS Intercomparisons and an "International Nutrients Scale System (INSS) in Sea Water"

11:00~11:30 David J. Hydes

User Requirements For Improved Determination Of Nutrients In Seawater: A Suggested Methodology For Improving The Traceability And Relative Accuracy Of Determination Of Concentrations Of Nutrients In Seawater

11:30~12:10 DISCUSSION

12:10~14:00 LUNCH

14:00~15:30 **SESSION 5 -- "International Nutrients Scale System" to establish comparability of nutrients data in the world ocean**
&SESSION 6 -- Discuss the future tasks on the use/development of chemical reference materials in ocean science
Co-chair: Patrick Roose & Andrew Dickson

15:30~15:50 COFFEE

15:50~17:20 **SESSION 6 -- Discuss the future tasks on the use/development of chemical reference materials in ocean science**
&
SESSION 7 -- General discussion
Co-chair: Michio Aoyama & David J. Hydes

ANNEXES IV ORGANIZATION

Michio AOYAMA / Meteorological Research Institute, Japan (Workshop Secretary)

Andrew DICKSON / Scripps Institution of Oceanography, USA

David J. HYDES / National Oceanography Centre Southampton, UK

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ANNEXES V

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ANNEX VI

LAB. TOUR PICTURES





