Intergovernmental Oceanographic Commission
Reports of Meetings of Experts and Equivalent Bodies

IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials (GESREM)

Third Session

Brussels, 22-24 September 1992

UNESCO

In this Series, entitled

Reports of Meetings of Experts and Equivalent Bodies, which was initiated in 1984 and which is published in English only, unless otherwise specified, the reports of the following meetings have already been issued:

1. Third Meeting of the Central Editorial Board for the Geological/Geophysical Atlases of the Atlantic and Pacific Oceans
2. Fourth Meeting of the Central Editorial Board for the Geological/Geophysical Atlases of the Atlantic and Pacific Oceans
3. Fourth Session of the Joint IOC-WMO-CPPS Working Group on the Investigations of 'El Niño' *(Also printed in Spanish)*
4. First Session of the IOC-FAO Guiding Group of Experts on the Programme of Ocean Science in Relation to Living Resources
5. First Session of the IOC-UN(OETB) Guiding Group of Experts on the Programme of Ocean Science in Relation to Non-Living Resources
6. First Session of the Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets
7. First Session of the Joint CCOP(SOPAC)-IOC Working Group on South Pacific Tectonics and Resources
8. First Session of the IODE Group of Experts on Marine Information Management
9. Tenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies in East Asian Tectonics and Resources
10. Sixth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration
11. First Session of the IOC Consultative Group on Ocean Mapping *(Also printed in French and Spanish)*
12. Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ships-of-Opportunity Programmes
13. Second Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources
14. Third Session of the Group of Experts on Format Development
15. Eleventh Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of South-East Asian Tectonics and Resources
16. Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets
17. Seventh Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration
18. Second Session of the IOC Group of Experts on Effects of Pollutants
19. Primera Reunión del Comité Editorial de la COI para la Carta Batimétrica Internacional del Mar Caribe y Parte del Océano Pacífico frente a Centroamérica *(Spanish only)*
20. Third Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources
21. Twelfth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of South-East Asian Tectonics and Resources
22. Second Session of the IODE Group of Experts on Marine Information Management
23. First Session of the IOC Group of Experts on Marine Geology and Geophysics in the Western Pacific
24. Second Session of the IOC-UN(OETB) Guiding Group of Experts on the Programme of Ocean Science in Relation to Non-Living Resources *(Also printed in French and Spanish)*
25. Third Session of the IOC Group of Experts on Effects of Pollutants
26. Eighth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration
27. Eleventh Session of the Joint IOC-IHO Guiding Committee for the General Bathymetric Chart of the Oceans *(Also printed in French)*
28. Second Session of the IOC-FAO Guiding Group of Experts on the Programme of Ocean Science in Relation to Living Resources
29. First Session of the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials
30. First Session of the IOCARIBE Group of Experts on Recruitment in Tropical Coastal Demersal Communities *(Also printed in Spanish)*
31. Second IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes
32. Thirteenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of East Asia Tectonics and Resources
33. Second Session of the IOC Task Team on the Global Sea-Level Observing System
34. Third Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets
35. Fourth Session of the IOC-UNEP-IMO Group of Experts on Effects of Pollutants
36. First Consultative Meeting on RNODCs and Climate Data Services
37. Second Joint IOC-WMO Meeting of Experts on IGOSS-IODE Data Flow
38. Fourth Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources
39. Fourth Session of the IODE Group of Experts on Technical Aspects of Data Exchange
40. Fourteenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of East Asian Tectonics and Resources
41. Third Session of the IOC Consultative Group on Ocean Mapping
42. Sixth Session of the Joint IOC-WMO-CCPS Working Group on the Investigations of 'El Niño' *(Also printed in Spanish)*
43. First Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Indian Ocean
44. Third Session of the IOC-UN(OALOS) Guiding Group of Experts on the Programme of Ocean Science in Relation to Non-Living Resources
45. Ninth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration
46. Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico
47. First Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Indian Ocean
48. Twelfth Session fo the Joint IOC-IHO Guiding Committee for the General Bathymetric Chart of the Oceans
49. Fifteenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of East Asian Tectonics and Resources
50. Third Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes
51. First Session of the IOC Group of Experts on the Global Sea-Level Observing System
52. Fourth Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean
53. First Session of the IOC Editorial Board for the International Chart of the Central Eastern Atlantic *(Also printed in French)*
54. Third Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico *(Also printed in Spanish)*
55. Fifth Session of the IOC-UNEP-IMO Group of Experts on Effects of Pollutants
56. Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Indian Ocean
57. First Meeting of the IOC *ad hoc* Group of Experts on Ocean Mapping in the WESTPAC Area
58. Fourth Session of the IOC Consultative Group on Ocean Mapping
59. Second Session of the IOC-WMO/IGOSS Group of Experts on Operations and Technical Applications
60. Second Session of the IOC Group of Experts on the Global Sea-Level Observing System
61. UNEP-IOC-WMO Meeting of Experts on Long-Term Global Monitoring System of Coastal and Near-Shore Phenomena Related to Climate Change
62. Third Session of the IOC-FAO Group of Experts on the Programme of Ocean Science in Relation to Living Resources
63. Second Session of the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials
64. Joint Meeting of the Group of Experts on Pollutants and the Group of Experts on Methods, Standards and Intercalibration
65. First Meeting of the Working Group on Oceanographic Co-operation in the ROPME Sea Area
66. Fifth Session of the Editorial Board for the International Bathymetric and its Geological/Geophysical Series
67. Thirteenth Session of the IOC-IHO Joint Guiding Committee for the General Bathymetric Chart of the Oceans *(Also printed in French)*
68. International Meeting of Scientific and Technical Experts on Climate Change and Oceans
69. UNEP-IOC-WMO-IUCN Meeting of Experts on a Long-Term Global Monitoring System
70. Fourth Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes
71. ROPME-IOC Meeting of the Steering Committee on Oceanographic Co-operation in the ROPME Sea Area
72. Grupo Mixto de Trabajo COI-OMM-CPPS sobre las Investigaciones relativas a 'El Niño' *(Spanish only)*
73. Fourth Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico *(Also printed in Spanish)*
74. First Meeting of the UNEP-IOC-ASPEI Global Task Team on the Implications of Climate Change on Coral Reefs
75. Third Session of the IODE Group of Experts on Marine Information Management
76. Fifth Session of the IODE Group of Experts on Technical Aspects of Data Exchange
77. ROPME-IOC Meeting of the Steering Committee for the Integrated Project Plan for the Coastal and Marine Environment of the ROPME Sea Area
78. IOC Group of Experts on the Global Sea-Level Observing System
79. Third Session of the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials

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IOC/-IAEA-UNEP/GESREM-III/3
Paris, 11 December 1992
English only

SC-92/WS-65

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1. OPENING OF THE SESSION

1 The Chairman of GESREM, Dr. W.D. Jamieson, called the meeting to order at 9 a.m. Tuesday, 22 September 1992. He welcomed the participants and thanked the GESREM members for their contributions towards the execution of the GESREM Work Plan during the intersessional period. He expressed gratitude to the Management Unit, North Sea Mathematical Models (MUMM) of the Belgian Ministry of Public Health and Environment and in particular Drs. G. Pichot and T. Jacques for offering to host the Meeting and for the excellent facilities provided.

2 Dr. T. Jacques standing in for Dr. G. Pichot who was unavoidably absent, welcomed the participants to Brussels and said his Unit of the Belgian Ministry of Public Health and Environment was honoured to be chosen as hosts for the Meeting. He described the activities of his Ministry in general and the Unit in particular, noting that there were great opportunities for future collaboration with GESREM and the GIPME Programme on account of certain similarities in the overall objectives of the GIPME Programme and the activities of his Unit. He wished the participants successful deliberations.

3 Dr. C. Ibe, IOC Technical Secretary, conveyed to the participants the warm regards and welcome of the Secretary IOC, Dr. G. Kullenberg. He said that it was remarkable that GESREM had accomplished in 1991/92 nearly all the objectives and targets specified in the GESREM Section of the Second GIPME Action Plan (1991-1993) adopted at the Seventh Session of GIPME (Paris, 21-25 January 1992). He pointed out the importance of keeping in view certain developments in discussing the future work of GESREM and referred specifically to the formalization of the IOC-UNEP Intergovernmental Panel on GIPME (Paris, 4-7 March 1992), and the outcome of the United Nations Conference on Environment and Development (UNCED) (Rio de Janeiro, June 1992) and in particular, Chapter 17 of Agenda 21, stressing the desirability to adjust the objectives and targets of the new GESREM workplan to the new realities and foci dictated by those events.

4 Dr. L. Mee, acting as Technical Secretary for IAEA and UNEP, welcomed the participants to the Meeting. He explained the importance of GESREM in the light of the decisions of the United Nations Conference on Environment and Development. GESREM provides a pragmatic service to the UN Member States by assuring a reliable supply of reference materials, an essential component of data validation strategies necessary for pollution control, and marine and coastal areas management. Without a constant supply of these materials, it would be impossible to master the status and trends of contamination and the effectiveness of management actions. Dr. Mee expressed his thanks to NOAA and in particular Dr. A. Cantillo for the continued production of the reference materials catalogue, another key GESREM activity.

5 The Chairman of the Committee for GIPME, Dr. N. Andersen, noted that, in the light of interventions by certain delegations during the Twenty-fifth Session of the IOC Executive Council (Paris, 10-18 March 1992), on the possibility of merging GESREM and GEMSI, it would be helpful if the Meeting would identify the uniqueness of its work plan in a way that demonstrates the need for its continuing as a separate entity, and describes its collaboration with the other GIPME groups of experts and its service to the marine scientific community.

6 The Chairman briefly introduced the participants. He pointed out that one of the reasons that influenced the choice of Brussels as the venue for the Meeting was the desire to enhance the participation of the staff of the Community Bureau of Reference (BCR), and promote closer collaboration between BCR and GESREM. The List of Participants is given as Annex III.

2. ADMINISTRATIVE ARRANGEMENTS

2.1 ADOPTION OF AGENDA

7 The Provisional Agenda for the Meeting which had earlier been circulated to the participants was adopted as the Agenda for the Meeting (Annex I).

2.2 DESIGNATION OF RAPPORTEUR

8 Dr. A. Walton was designated as Rapporteur.

2.3 CONDUCT OF THE SESSION

9 The IOC Technical Secretary informed the Meeting of the arrangements for the Meeting including the time-table and introduced the available documentation.

3. STATUS OF ON-GOING GESREM ACTIVITIES

3.1 PREPARATION OF REFERENCE MATERIALS GESREM 1 AND GESREM 2

3.1.1 GESREM 1

10 Dr. T. Gills reported on the status of GESREM 1 (RM 8044 in NIST nomenclature) for Trace Elements in Freeze-Dried Mussels. Approximately 72 kg (gross weight) of freeze-dried mussels was received from Monaco and processed using a Waring type blender/cutter and the NIST jet milling facility. The material was then blended and stored in plastic lined boxes. The 72 kg base material had a final process weight of 53.7 kg of a finely powdered material. This yielded into approx. 2,100 x 25 g units of bottled material.

11 It is envisioned that RM 8044 will be certified for 30-40 elements of interest to marine scientists using the independent methods approach employing techniques and methods commonly used in marine and environmental analyses. Certification and/or value assignment of the elemental concentrations will be a joint effort between IAEA, NRC, NIST and others. Information on several organic pollutant concentrations will be provided as non-certified values.

12 The following approaches will be undertaken to ensure that the certification of RM 8044 can be achieved in an orderly and timely manner:

(i) Investigation of matrix specifications including the determination of moisture content, particle size distribution, and drying weight loss. [CBNM-Kramer]

(ii) Derivation of a statistical scheme for assessing material homogeneity and developing certification protocols (NIST, NRC [Gills/Schiller/Berman])

(iii) Bottling the 53.7 kg of the powdered mussel into specially cleaned glass bottles [NIST (Gills)]

(iv) Assignment of analytical tasks along with analysis protocols for analysis that include but not limited to the following:

a. recommended drying procedures
b. minimum sample sizes
c. reports of analysis (composition and data format)
d. error budget

(combined effort of IAEA, CBNM, NRC, NIST and NIES)

(v) Data assessment and assignment of certified values (combined efforts of IAEA, CBNM, NRC, NIES, NIST)

(vi) Report writing and certificate writing (combined efforts of IAEA, CBNM, NIES, NRC, NIST)

(vii) Marketing Strategy/Sample Distribution

3.1.2 GESREM 2

13 Dr. R. Dawson reported on the progress to date in the preparation of a freeze-dried mussel tissue GESREM-2 (RM 8045 in NIST nomenclature). He reminded the Group that one of the reasons for preparing this material was in support of the International Mussel Watch Programme. Hence, the reference material was specifically intended for the analysis of chlorinated hydrocarbon pesticides and PCBs.

14 It was also originally decided that the material should preferably contain relatively high levels of contaminants. A team of scientists from the University of Maryland and NOAA reviewed data from previous mussel collections by the NOAA Status and Trends Programme and determined that a site in the N.Y. Harbour area would be appropriate.

15 The collection was conducted in December 1991 and was hampered by severe weather and an unexpected depletion of the mussel population. Consequently, a mixture of Modiolus and Mytilus (ribbedmussel and blue mussel) was gathered in an attempt to gain a sufficient quantity of material.

16 Unlike the GESREM 1 sample which was commercially obtained, the logistic problems and the time-consuming efforts to shuck mussels with a limited team of people, meant that after bulk freeze-drying yielded only 5 kg of material which was transferred to NIST for homogenization and characterization.

17 The material remaining was blended and homogenized at the University of Maryland. Some 50 bottles of 7g dry weight each resulted, of which 38 were provided to the International Mussel Watch Project Office in Woods Hole Oceanographic Institution, Massachusetts, U.S.A. These samples are to be analyzed by laboratories in South and Central America in an intercomparison exercise organized by the International Mussel Watch. In addition to the intercomparision sample, the laboratories have received solutions of pure analytes, other CRMs and a comprehensive selection of relevant literature. At the same time intercomparison samples were provided to the analytical laboratories at Texas A & M and IAEA-Monaco. In addition, material was sent to a lead laboratory in Indonesia in anticipation of wider participation as an extension of the International Mussel Watch Project to the Pacific Rim. The intercomparison sample was also analyzed by ICP-MS for a suite of metals at the Skidaway Institute and for PAH, chlorinated hydrocarbon and lipid content at the University of Maryland.

18 It is clear from the provisional results that the material is a fairly good sample for PCB analysis being relatively high (ca. 500-600 ppb) in total PCB with a clearly discernable Aroclor 1254 plus 1260 pattern of congeners. However, the organochlorine pesticide content (with the exception of DDE) may be moderately low and hence more analytically challenging.

19 The Group discussed the difficulties and costs in obtaining large amounts of mussel tissue and also recognized that it was difficult to get contaminated shellfish from commercial sources. Dr. Gills also pointed out that commercially grown mussels produced a much more homogeneous powder with fewer pieces of debris. The wild populations gathered for GESREM-2 were not depurated, grew in the sediments of the area and hence contained more debris. A small subgroup was formed to decide whether additional collections should be made for another GESREM reference material and to discuss the feasibility of substituting other tissues. This Group concluded that another attempt must be made to collect a contaminated mussel tissue for certification. Approximately 30 kg freeze-dried weight of material is needed. To avoid confusion with the existing GESREM 2 (RM 8045), this material should have an interim designation of GESREM 3.

20 Due to the limited amount of material, GESREM 2 (RM 8045) will be designated as a quality control reference sample for use in assessing measurement capability and in method development. Approximately 4.7 kg was obtained as a jet-milled product and is expected to yield 300 x 15 g units for organic analysis. RM 8045 can be especially useful to researchers in developing countries who may be analyzing similar matrices for the first time and who may need to gain further experience in both sample treatment and analyses to achieve precise and accurate results. The general approach for characterizing RM 8045 will be similar to that for RM 8044 using available organic analysis capabilities at IAEA, NRC,

NIST, and the University of Maryland, U.S.A. RM 8045 will be analyzed for selected PAHs, polychlorinated biphenyls, chlorinated pesticides, and several toxic inorganic elements. The values assigned will be recommended values with some estimation of error.

21 The organic reference material will be accompanied by a report that is designed to document all related analytical procedures with enough detail that will allow some degree of instructional training for users. The IAEA will handle the distribution of RM 8045, although NIST will retain a small quantity of the material for methods development and limited sales.

3.2 FINAL DRAFT OF THE SECOND UPDATE TO THE REFERENCE MATERIAL CATALOGUE

22 The third edition of the catalogue titled '*Standard and Reference Materials for Marine Science*' is currently available (A.Y. Cantillo, NOAA Tech. Memo 68, 577pp.). The types of materials included are ashes, gases, oils, rocks, sediments, sludges, soils, tissues and waters, instrumental performance evaluation materials and physical properties materials. Source, description and preparation, analytes and values, cost, references and comments are given for close to 2,000 reference materials. Registry numbers are listed for most analytes. Selected organic compound structures are provided. Indices are available to facilitate searches by matrix or analyte. The catalogue is also available in electronic form as Macintosh WORD 4.0 documents. Reprinting of the document as an IOC-UNESCO publication and conversion to IBM PC-compatible format will be explored.

3.3 WORK BOOK ON THE PROPER USE OF STANDARDS AND REFERENCE MATERIALS

23 A Working Group convened under the Chairmanship of Dr. S. Berman recognized that the document produced by Dr. T. Wade (University of Texas A & M) was still in draft form and subject to further amplification. Before proceeding to the final document the WG felt it appropriate to have a further discussion in GESREM on the objectives of the manual so as to ensure the appropriateness of the final document.

24 Dr. Calder reviewed the original objectives for the Workbook as determined at the second Meeting of GESREM and revised in subsequent meetings of the GESREM core group. The Workbook is intended to provide guidance and examples for the proper use of standards and reference materials throughout the total analytical process. This includes instrument calibration standards, internal standards, working standards, and certified reference material. To provide a degree of focus it was agreed that the examples given in the Workbook should relate to the International Mussel Watch Project and refer to the determination of organochlorine compounds. The Workbook is not intended as an analytical methods manual or a complete quality assurance/quality control plan.

25 The working group under Dr. S. Berman's leadership will continue its work intersessionally.

4. THE COMMUNITY BUREAU OF REFERENCE (BCR)

26 An enormous number of analyses are being performed every year for the purpose of monitoring the environment. The determinants to be measured are not only numerous but also very diverse; the complexity of the matrices to be studied represents another analytical difficulty. In order to ensure that the results are comparable within the European Community, e.g., for controlling the application of EC directives or drawing of conclusions from monitoring campaigns, the harmonization of the analytical capabilities of the laboratories in all the Member States has to be achieved. Accuracy is a prerequisite of analysis; it can be verified by using suitable CRMs and by participating in intercomparisons.

27 The Community Bureau of Reference (BCR) of the Commission of the European Communities has the task to improve the results obtained throughout the European Community. One of the major tools to achieve this goal is the organization of intercomparisons; these exercises are carried out when analytical problems are recognized and highlighted by the Member States. They often allow a stepwise approach; the analytical methods used for the determination of chemical forms of elements are based on successive

steps which may vary from one procedure to another. Each step of the analytical procedure should be examined separately to verify the laboratory's performance and detect and evaluate the sources of error which may arise. This should allow each participant to finally validate his method as applied in his laboratory and possibly to investigate its ruggedness. To do so, different samples, previously characterized for their homogeneity and stability, are prepared and sent to the participating laboratories. Typical matrices are:

(i) solutions containing one or several analytes including potential interfering compounds to evaluate the performance of the final detection including quantitation of the separation techniques;

(ii) cleaned extracts to fully test the performance of the separation on real samples;

(iii) raw extracts to verify the clean-up procedure;

(iv) real matrices homogeneously spiked and equilibrated with the analyte(s) to be determined to test the total analytical procedure;

(v) real samples.

28 These different steps enable the identification of the sources of error and consequently help the laboratories to remove them. The results of these exercises are discussed in technical meetings with all the participating laboratories. Such intercomparisons may also enable the elimination of any bias linked to a certain methods. Systematic errors such as contamination, losses, incomplete extraction, decay of compounds, calibration error, etc. can be identified by comparing different (pre) treatment procedures (e.g., solvent and acid extraction), separation techniques (GC, LC) and final detection (e.g., AAS, ICP, MS, etc.).

29 Once the laboratories are in good control of their different validated methods, a certification can be contemplated to disseminate the gained expertise and to obtain results that are comparable. The CRMs produced are as similar as possible to real matrices in order to be representative of the analytical difficulties encountered in the analyses of environmental samples. They are made available by the Commission of the European Communities along with a certification report describing their preparation, the homogeneity and stability studies, the analytical methods used and the certified values. A CRM is thus a material which disseminates the experience collected by those laboratories which improved the quality of their measurements in a number of intercomparisons and demonstrated their accuracy. CRMs are therefore considered as the conclusion of collaborative projects, enabling a wide dissemination of results to be achieved (not only within the EC but also on a worldwide basis).

30 A series of CRMs have already been produced by the BCR for the quality control of analysis of samples from the marine environment. This list is given in the BCR-catalogue and covers a list of elements/compounds (e.g., trace elements, PCBs) in various matrices (e.g., mussel, cod mussel, sediment, seawater...). Other projects are currently going on, related to the marine environment, particularly:

(i) certification of Hg in seawater;
(ii) certification of trace elements in estuarine water;
(iii) certification of MeHg in tuna fish;
(iv) certification of butylins (MBT, DBT and TBT) in a coastal sediment;
(v) seawater microbiology (intercomparisons).

31 Another ambitious project which is likely to start very soon deals with the quality assurance of marine environmental monitoring. The quality assurance and quality control requirements for the chemical measurements of the mandatory determinants in the Marine Environmental Monitoring Programmes (MEMPs) of the North Sea Task Force (NSTF) and the Joint Monitoring Group of the Oslo and Paris Commissions are of paramount importance. The project QUASIMEME (Quality Assurance of Information in Marine Environmental Monitoring in Europe) has received the approval of, or the attention from, the Commission of the European Communities, the OSPARCOM and the Barcelona and Helsinki Conventions;

it is a holistic approach that will cover quality management, proficiency testing, learning programmes and communication. The project will co-ordinate the development of the quality measurement and Quality Assurance management for some 80 laboratories who contribute data to the MEMPs; it will involve frequent round robins, the availability of common RMs, the production of additional CRMs and intercomparisons on the technical aspects of sampling and sample storage. The parameters and target matrices are : chlorinated compounds (CB 28, 52, 101, 118, 138(+163), 153, 105, 156, 180) in fish oil, trace metals (Cu, Zn, Pb, Hg, Cd) in sediment and nutrients (NO_3, NO_2, PO_4, NH_4) in seawater.

32 GESREM felt it important that information concerning its objectives, workplans and recommendations need to be more widely disseminated among marine institutions, including BCR. In this way, the activities of the Group (which includes among its memberships the major producers of standards and reference materials), and its identification of existing needs in marine science will become known, thereby minimizing duplication of effort in the production of these expensive materials and giving a sense of priorities in what needs to be developed.

5. REVIEW OF STATUS AND NEEDS FOR NEW REFERENCE MATERIALS

33 Prior to reviewing the listed agenda items, GESREM producer organizations presented their plans for future work. These are summarized in Annex IV.

5.1 INORGANIC NUTRIENTS IN SEAWATER

34 The need for a set of certified standards for inorganic nutrients in seawater was discussed in the light of global and regional research programmes. International programmes such as JGOFS and WOCE will be carried out over the next 5-8 years and suitable reference solutions for open-ocean concentrations of phosphate, nitrate, nitrite, ammonia and silicate are required. It was noted that although individual standards and spikes exist, a reliable seawater certified reference material does not exist and high priority should be given to its development. Dr. P. Ridout from Ocean Scientific International (U.K.) presented an overview of a product just developed and soon to be released which comprises a natural oceanic seawater with depleted levels of nutrients. It was stressed that this product is a research material only that may be useful in the preparation of spiked standards. Development of a stable seawater standard for low level nutrient concentrations continues to be researched by Dr. A. Aminot (IFREMER, France). This latter material is not expected to be prepared in enough quantity to satisfy institutions working outside the context of the Project QUASIMEME of the European Community. It is also not likely to be certified for silicate because of the preparative techniques being employed.

5.2 THIOSULFATE FOR WINKLER TITRATIONS

35 The Group agreed it was unnecessary to consider the development of a reference material for thiosulfate.

5.3 PIGMENTS AND ALGAL CULTURES

36 Dr. Dawson described the history and developments in the analysis of photosynthetic pigments in seawater. The solutions provided in the EPA programme are primarily designed for the analysis of total chlorophylls by absorbance and fluorescence spectrophotometry. This material is not suitable for HPLC analysis since the solutions degrade with time and the carotenoid profile is limited.

37 SCOR Working Group 78 has held a number of practical workshops and an intercalibration exercise. An extensive monograph on the subject is to be produced shortly. The approach adopted by SCOR does not necessarily rely on the availability of pure standards or certified reference materials, but rather on characterization of a standard suite of algal cultures, determination of accurate extinction coefficients and extensive studies of storage effects, extraction, etc.

38 An NSF sponsored three round intercalibration exercise organized by Dr. Bidigare (University of Hawaii) involved analyzing a large suite of chloropigment and carotenoid standards in solvents stored

at -20°C. Only a few laboratories participated but with good agreement. Studies were also conducted on the stability of the compounds which varied according to molecular structure.

39 In other areas, internal standards canthaxanthin (SCOR) and Zn-butylpheophorbide-a (NSF via Dr. Repeta) have been proposed and are urgently needed. These should preferably be stable and exhibit visible and fluorescence characteristics similar to chloropigments and carotenoids.

40 Dr. Repeta (Woods Hole Oceanographic Institution), during the course of the JGOFS cruises, has reported successes in using prepared, isolated carotenoids at sea after they had been frozen in benzene at -20°C. Given the ever increasing use of chemotaxonomy, including the discovery of divinyl chlorophyl derivatives in prochlorophyte populations, it is difficult to specify all the pigments which ideally should be available as pure standards or certified materials.

41 Certainly accurate extinction coefficients and a few primary standards may go a long way to satisfy the basic requirements of a Quality Assurance programme for pigment analyses and clearly a combination of approaches will be required.

42 Scientists at NIST are currently trying to obtain accurate extinction coefficients on a number of carotenoids in foods. Discussions are underway concerning the development of other matrix-based reference materials. A SRM 2382 (carotenoids and vitamins in food) is currently in preparation. This could feasibly be expanded, depending on the results of the stability studies, to include some marine derived carotenoids. There is, therefore, an obvious need for the following (non-exhaustive) list of compounds *:

fucoxanthin	from	diatoms or Sargassum
peridinin	from	dinoflagellates
lutein	from	spinach
zeaxanthin	from	blue green algae
alloxanthin	from	cryptomonads
chlorophyll c	from	Sargassum
prasinoxanthin	from	prasinophyte
19'hex-fucoxanthin	from	prymnesiophytes
19'but-fucoxanthin	from	chrysophytes
α-carotene	from	Sigma
B-carotene	from	Sigma
violaxanthin	from	daffodil petals
chlorophylls a and b	from	Sigma
divinylchlorophyll a and b	from	Prochloron cultures

* for further details see Wright et al 1991 and modifications thereof.

43 Information provided by Dr. Kraft of NIST suggested that once some materials are available, round-robin analyses on unknown samples could be organized.

5.4 ALGAL TOXINS

44 Occurrences of toxic poisons in the marine environment in various parts of the world appear to be more frequent. Recent advances in mass spectrometry have greatly facilitated the capacity to analyze for these groups of compounds (all of the paralytic, diarrhetic and amnesic shellfish poisoning toxins), in a much more definitive way than the rather more frequently used mouse bioassay techniques (used also in a regulatory setting). The IOC-FAO International Programme on Harmful Algal Blooms has indicated considerable interest in GESREM's initiative to encourage the preparation of suitable reference materials. Additionally, mouse bioassay procedures are becoming less and less acceptable as an analytical approach to toxicity problems - thus amplifying the need for suitable standards for immunoassay approaches. Canadian laboratories appear to be alone in this activity which GESREM considers as high priority.

5.5 CARBON DIOXIDE IN SEAWATER

45 Previous discussions in GESREM considered this problem to be of high priority. In the light of the large scale international oceanographic programmes, e.g., JGOFS and WOCE, a series of standards have been prepared by Dr. A. Dickson (Scripps Institute of Oceanography) for total dissolved inorganic carbon measurements in seawater and are available on a limited basis. These materials may also be used as alkalinity working standards. The standards appear to be stable and have been used in a collaborative study among 14 laboratories and on research cruises undertaken by scientists from several countries. Production on a wider scale is now feasible and Dr. Dickson has indicated his willingness to work with a major standards supplier to achieve distribution and world-wide use of such materials. Ocean Scientific International (OSI) and NIST expressed their interest in such co-operative development. The need for certified reference materials for other carbon system parameters (e.g., alkalinity, pCO_2, pH) still exists. Research on the production of these materials is continuing at Scripps.

5.6 NON-PERSISTENT PESTICIDES IN NATURAL MATRICES

46 The use of "non persistent" pesticides including carbamates, organo-phosphorus compounds, etc. is increasing on a world-wide basis. Analytical techniques adapted to environmental materials have not advanced as rapidly as desired and there is a clear lack of relevant standards and reference materials - particularly for the marine environment. A GEEP-GEMSI workshop is planned in Mazatlan, Mexico for 1993, in order to examine the marine environmental significance of these compounds and the feasibility of incorporating them in routine contaminant monitoring programmes. This builds upon an ongoing IAEA-CEC-UNM (National University of Mexico) project in Mazatlan which has already quantified gradients of some organophosphorus pesticides and examined their food-chain dynamics and association with particulate material.

47 A number of compounds were cited which warrant environmental concern. Contrary to the assumption of "non-persistence" in water, these have been found to exhibit long residence times in a number of sediments. These include organophosphorus (pyrethroid) insecticides, triazine pesticides, herbicides such as paraquat and glyphosate, N-methyl carbamates and urea pesticides (e.g., DIMILIN). Many of these are only available as instrument calibration standards. Preparation of CRMs will require a considerable amount of laboratory work to examine the stability of these compounds in a variety of matrices and a study of the intercomparability of analytical techniques employed (particularly sample extraction procedures).

48 The choice of standards is somewhat method dependent. For example, determination of carbamates by HPLC-post column hydrolysis/post column OPA adduct fluorescence detection would permit determination of the following compounds for which standards would be required:

aldicarb sulfoxide
aldicarb sulfone
oxamyl
methomyl
hydroxycarbofuran
aldicarb
carbofuran
carbaryl
napthol

49 It was noted that a method based on lc-ms was developed recently for the determination of N-methyl carbamate pesticides. (An Evaluation of Atmospheric Pressure Ionization Techniques for the Analysis of N-methyl Carbamate Pesticides by Liquid Chromatography with Mass Spectrometry, by S. Pleasance, M.R. Bailey, D.H. North and J.F. Anacleto, in J. Amer. Soc. Mass Spectrom. 3, 378-397 (1992).)

5.7 SEDIMENT ANCILLARY PARAMETERS

50 After discussion, the Group does not recommend development of special reference materials for these measurements, but does recommend that such properties be measured and reported as frequently as possible for all sediment-based CRMs.

5.8 METABOLITES OF PAHs

51 The Group felt that it was not in a position at this stage to examine possible reference materials in any detail. On the other hand it felt that considerable study was necessary of a number of identifiable metabolites, with the objective of arriving at a list of priority compounds. The Group offered its analytical expertise in this evaluation process.

52 Dr. Dawson volunteered a preliminary listing of potential PAH metabolites of concern based on an examination of the National Cancer Institute Repository listing. Benz(a)pyrene metabolites likely to be produced by marine organisms and to exhibit biological effects include the 7,8 dihydrodiol (cis from microbial and trans from animal respectively) 9,10 dihydrodiol (cis or trans) 7,8,9,10 tetrahydrotetradiol, 3-OH benz(a)pyrene, 9-OH benz(a) pyrene and 3,6-quinone. A similar list of benzanthracene metabolites could also be envisaged. He noted that GEEP may also assist in compiling a list of target analytes.

5.9 METHYL MERCURY COMPOUNDS

53 The importance of studies on exposure of human populations to mercury through excessive consumption of food (particularly fish) is well known. The apparent general increase of mercury in the global environment has highlighted the potential importance of anthropogenic mercury emissions, especially from fossil fuel combustion. During the last decade it was shown that a more widespread air pollution and long-transport of mercury from point source discharges have taken place. This has caused substantially increased mercury concentrations in lake fish, in many cases exceeding maximum permissible levels of mercury by a factor of 2 or more. This is mostly a problem in Sweden and North America. In addition, many local areas all over the world are heavily polluted due to the massive Hg contamination by chloralkaline plants in the past. Under natural conditions inorganic mercury can be transformed into very toxic methyl mercury compounds, which bioaccumulate. The amount and toxicity of mercury in human foods is therefore controlled by complex ecological and biogeochemical processes. Existing knowledge of these processes is inadequate to assess the environmental impact on human health, but current research shows promising advances. In areas that are already polluted (e.g., Amazon Region in Brazil) or contain elevated natural levels (e.g., Mediterranean Basin) of inorganic mercury, it is extremely important to perform a good monitoring programme for inorganic and methyl mercury compounds. This is supported by the fact that, if conditions that favour methyl mercury formation are established (low pH, higher temperature, appropriate sulfide concentration, etc.) as a result of climate change or an increase in organic load to the water body, methyl mercury concentrations in some organisms would reach levels that are far above these that are permissible.

54 At the latest International Conference on "Mercury as a Global Pollutant" (Monterey, California, June 1992) it was concluded that many questions on the biogeochemical cycle of mercury in the natural environment have been answered, but there are still a lot of gaps for its total understanding. One of the most important research contributions is the availability of specific and sensitive analytical methods, by which it was possible to perform studies under natural conditions.

55 It is obvious that a good quality assurance programme should be implemented in many of such studies. One way to control the accuracy of the results is by analyzing RMs. At present there are many CRMs available for total mercury concentration in various matrices (sediment, soil, ash, water, and tissue).

56 Unfortunately, only 4 marine RMs are certified for methyl mercury. These are available from the National Research Council of Canada (NRCC). As follows:

DOLT-1, Dogfish Liver, (80+/-11 µg MeHg.kg^{-1} as Hg)
DORM-1, Dogfish Muscle, (731+/-60 µg MeHg.kg^{-1} as Hg)
TORT-1, Lobster Hepatopancreas, (121+/-14 µg MeHg.kg^{-1} as Hg)
LUTS-1, Non Defatted Lobster Hepatopancreas, (9.3+/-0.6 µg MeHg.kg^{-1} as Hg)

57 Results are given as certified value +/- 95% confidence interval. According to the latest news from NRCC, DOLT-1 is no longer.

58 NIES is currently certifying a human-hair sample for methyl mercury.

59 It is understood that these materials are not sufficient to satisfy the quality assurance control requirements in many laboratories performing methyl mercury analyses. Therefore, apart from the analysis of certified RMs, the accuracy of analytical procedures for determination of methyl mercury were tested by intercalibration exercises as well as comparison of the results obtained by various isolation and final measurement procedures (especially in the laboratories with good experiences in methyl mercury analysis).

60 A few studies of the effects of some physical parameters (UV light, gamma irradiation, freeze-drying, long-term storage) on the stability of methyl mercury in biological and sediment samples have already been performed. The results of these studies showed that methyl mercury is very stable in most of the matrices studied. In some currently available biological CRMs for total mercury, methyl mercury was also determined by a few laboratories using different analytical procedures. Very good agreement of the results was obtained. In addition, methyl mercury was shown to be very stable under good long-term storage conditions. The time has now come to produce new RMs for methyl mercury with much tighter confidence intervals.

61 Since large numbers of laboratories world-wide perform methyl mercury analysis using various improved separation and detection techniques, its certification should not be a problem in the future. It is therefore suggested that each new reference material certified for trace elements should also be certified for methyl mercury. In addition, RMs that are already certified for total mercury can also be recertified for methyl mercury, but only where they are available in large stocks. This would definitely help many laboratories that have just started with methyl mercury analysis as well as those that have long-term experience in this matter.

5.10 ICP - MS TRACE ELEMENT STANDARDS

62 No special standards were believed to be necessary at this stage.

5.11 PLANAR POLYCHLORINATED BIPHENYLS

63 In the certification of materials for PCB's, the Group urged producers to attempt to present as much information as possible on the levels of coplanar congeners. It was noted that multi-dimensional GC is capable of resolving these, and that recent advances in shape recognition chromatography may be useful in separating planar from non-planar congeners.

5.12 DISSOLVED ORGANIC CARBON (DOC)

64 National and international programmes related to further elucidation of the carbon cycle demonstrate clearly the need for a certified reference material for DOC. The fact that the parameter is also of fundamental importance in chemical and biological oceanography further supports this requirement. Recent progress in analytical methodology seems to suggest that such a development probably is feasible in the near future.

6. NEEDS IDENTIFIED BY OTHER GROUPS

6.1 GIPME GROUPS OF EXPERTS ON METHODS, STANDARDS AND INTERCALIBRATION (GEMSI) AND ON THE EFFECTS OF POLLUTION (GEEP)

65 Dr. Knap provided a review from the GEMSI perspective and recognized the effectiveness of GESREM's role in promoting co-operative efforts between producers of reference materials and marine scientists. From a GEMSI point of view, the community is now in better shape with regard to RMs in the "contaminants category". There are generally good standards for trace metals, organochlorines and PAH's. Dr. Knap referred to Dr. Dawson's statements on RM needs in relation to the International Mussel Watch Programme, i.e., PAHs, chlorinated pesticides and chlorobiphenyls. The present directions of GEMSI are to continue with having intercalibiation exercises for the above three groups of compounds and to expand efforts into methods, training and intercalibration for JGOFS programmes. A JGOFS protocol manual has been developed and various needs for reference material and certified standards have been suggested. There is a great need for materials for inorganic nutrients in seawater such as phosphate, nitrate/nitrite, silicate and ammonia. Dr. Knap mentioned the CO_2 intercomparison exercises being carried out by Dr. A. Dickson (SCRIPPS Institute of Oceanography, La Jolla, CA, USA). Many of the analysts are now moving to seawater equilibrations for pCO_2 which is instrument specific and soon there will be a pCO_2 instrument intercomparison exercise. One identified need is a certified solution for alkalinity. For pigments analyzed by HPLC there is a need for a seawater reference material for various pigments. Looking to the future, GEMSI will be expanding its activities and placing more emphasis on modern pesticides and algal toxins. It will look to GESREM for development of the reference materials that will be required to support these efforts.

6.2 UNITED NATIONS ENVIRONMENT PROGRAMME (UNEP)

66 No additional needs were identified.

6.3 INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA)

6.3.1 Review of Intercalibration Exercises Organized by MESL on Behalf of IOC, IAEA & UNEP (since 1990)

67 The UNEP Regional Seas Programme now covers over 120 countries in 11 geopolitical regions. In near future it will also expand to two new regions: the Black Sea and North West Pacific. Many regional action plans include a strong component of marine pollution assessment, control and abatement. The IOC programme of GIPME, which is now co-sponsored by UNEP, conducts global and regional pollution assessments and provides a forum for technical expertise. For its part, IAEA runs the only marine laboratory in the UN system and provides quality assurance services worldwide for nuclear and non-nuclear measurements in the marine environment.

68 The Marine Environmental Studies Laboratory (MESL) of IAEA-MEL in Monaco has conducted intercomparison exercises on trace organic compounds and trace elements since 1970 as a part of its contribution to IAEA's Analytical Quality Control Service (AQCS) and UNEP's Regional Seas Programme and occasionally in association with the IOC-UNEP GIPME programme. Results of previous exercises have revealed serious problems for many regional laboratories to obtain comparable data. This, in turn, has raised serious concerns on the validity of region-wide or global marine pollution assessments. Even more worrisome was the apparent lack of improvements in data quality from exercise to exercise.

69 As a consequence of the above situation, it is necessary to seek increased support for quality assurance programmes. Staff of MESL, with funding from UNEP, the World Bank and regional trust funds, embarked on a campaign to train analysts in modern measurement techniques and to supply appropriate instruments in Member State laboratories. For example, in the Mediterranean, a comprehensive approach has been adopted (with support from UNEP and the World Bank) which includes specialist training, the provision of analytical instruments, and instrument maintenance services, joint

monitoring expeditions and regular follow-up with intercalibration exercises and split-sample analyses. As a result some laboratories have participated in the latest intercalibration exercise organized by IAEA and UNEP on organic contaminants in the sediment IAEA-357 (described below) for the first time.

70 Another difficulty faced by many analysts starting to conduct studies of marine contamination is finding a reliable method which uses easily available instruments. For this purpose, UNEP introduced its "Reference Methods for Marine Pollution Studies" series in 1983. The responsibility for editing the "Reference Methods" series was assumed by IAEA's Monaco Laboratory in 1984 (in co-operation with several specialist UN Agencies) and the series now include over 60 volumes, available free of charge world-wide. Scientific review of the methods is co-ordinated by another international expert group, GEMSI (the GIPME Group of Experts on Methods, Standards and Intercalibration). These methods are not obligatory but represent a reliable fall-back position, cover a wide range of themes including microbiological analysis, monitoring strategies, sampling, chemical analyses, biological effects measurements and quality assurance/quality control. Methods are continuously being updated, and work is now continuing on the development of new methodologies for organophosphorous pesticides, herbicides and fungicides. This will certainly facilitate the widest possible participation in the upcoming pilot studies for these parameters. Amongst the parameters that should also be studied are indicators of sewage pollution - fecal sterols. More research should also be performed for possible preparation of new reference materials certified for a wider list of parameters (especially organophosphorous pesticides and fecal sterols).

71 In light of the expansion of the Regional Seas Programme activities to new regions worldwide (eg. the Black Sea and the North West Pacific) and the increasing number of parameters to be studied, there will be a concomitant increase in the demand for the preparation of new reference materials. This is a controversial situation, since it is well known that resources are decreasing while demands for new reference materials are increasing. The role of GESREM will be vital in ensuring a close co-operation between the producers and avoiding unnecessary programmatic overlaps.

72 Recently two intercalibration exercises have been completed. The results are reported in two documents.

1. "Worldwide Intercomparison of Trace Elements in Marine Sediment SD-M-2/TM", IAEA/A1/053, Vienna; *prepared by L.D. Mee and B. Oregioni, 1991.*

73 The first intercalibration exercise was organized for analyses of trace elements in a deep sea sediment. This sample represents a "baseline sample" for marine pollution chemists. The exercise was designed to satisfy the requirements of participants in the IAEA's AQCS as well as UNEP's Regional Seas Programme and similar activities conducted within the auspices of GIPME.

74 This intercalibration exercise attracted the largest number of participants yet gathered for an IAEA-UNEP marine sediment intercomparison. In total, 121 laboratories from 5 countries reported their results for up to 62 elements. As a result, 33 elements could be given A and B class consensus certification, which is a considerable improvement over previous exercises. Unfortunately, only a small stock is still available for distribution as a RM, due to heavy demand for this material during the exercise. However, participants in the intercalibration exercise have retained their sample material as an RM - which is very valuable indeed!

75 Results obtained by different analytical techniques and digestion methods were also compared in the report. Graphical evaluation was made for parameters when consensus values were not closely achieved in order to find out the source of systematic errors. For the purpose of certifications as a RM, the median values were classified following tighter criteria than those used in previous exercises.

76 A new intercalibration for trace elements intercomparison exercise is in progress using IAEA-356 "polluted" sediment from the Venice Lagoon. The results are due at the end of October 1992, while the report should be completed by the end of 1992.

2. **"Worldwide and Regional Intercomparison for the Determination of Organochlorine Compounds and Petroleum Hydrocarbons in Sediment Sample IAEA-357", UNEP/IOC Report (No. 51),** *prepared by J-P. Villeneuve and L.D. Mee, 1992.*

77 The second report describes the results of IAEA-UNEP Intercalibration run IAEA-357 for chemical analyses of organochlorine compounds and petroleum hydrocarbons in a marine sediment sample collected from a polluted coastal area (the Venice Lagoon - Italy). A total of 32 laboratories eventually participated in the exercise of which 12 were participants in the MEDPOL programme, 6 from CEPPOL (Wider Caribbean) programme and 3 in the ROPME programme and 11 from other regions of the world.

78 The exercise has permitted (i) the identification of those laboratories having continued difficulties in obtaining accurate and precise data, and (ii) the establishment of reference values for several compounds which has allowed this material to be certified as a reference material as a part of the IAEA's AQCS programme.

79 Despite considerable improvements in data quality in general, the data for some basic parameters remain surprisingly poor. The report discusses difficulties in interpretation of parameters such as "total oil", "total aliphatics" or "total aromatics" which are rather "method specific" and difficult to calibrate. Measurements using the fluorimetric technique (commonly employing chrysene as a standard) are very "method specific" and small variations in the wavelengths and slit widths employed result in poor precision (CV for total petroleum hydrocarbon as the fluorimetric chrysene equivalent, was 74 %). The gas chromatographic alternative of measuring the "unresolved complex mixture" is not much better. On the other hand, some specific oil component and PAHs can be measured with excellent precision (better than 20 %).

80 It is suggested that much more attention should be directed toward these measures of contamination. "Method specific" techniques should be avoided for environmental studies but if a technique is recognized as being "Method specific" then the basic methodological constraints should be stated as part of the measurement. It should also be examined whether chrysene is the most appropriate standard for wide use and the search should be continued for a new robust measure of total petroleum hydrocarbons.

81 New intercomparison exercises for organic contaminants in biota are planned for late 1992.

6.4 INTERNATIONAL COUNCIL FOR THE EXPLORATION OF THE SEA (ICES)

82 ICES remains interested in eutrophication and its consequences. Accordingly, there is a demand to improve the standardization of nutrient determinations in marine and fresh water. Reference materials for nutrients would be extremely useful to ICES and its Member States.

83 Because of the adoption of ethoxyresorufin-O-deethylase (EROD) as a biological effects measurement technique in the North Sea Monitoring Master Plan and some problems that have been experienced with resorufin standards for this measurement, the preparation of a resorufin standard would also be useful.

84 There continues to be a need for increased certification of chlorobiphenyl congeners in marine materials (sediments and biological tissues) with increased emphasis on co-planar CBs.

6.5 JGOFS, WOCE, GLOBEC

85 JGOFS requirements have in general been discussed under other agenda items, as have those of WOCE.

86 GLOBEC is a programme similar to JGOFS but with the emphasis more related to ecology. Needs in this programme pose problems at present considered beyond the context of the current activities of the Group.

7. GESREM WORK PLAN FOR 1993-1997

7.1 ACTION ITEMS AND MEMBERS RESPONSIBLE FOR THEIR IMPLEMENTATION

A. Ongoing Actions

1. Proceed with certification of GESREM 1 for a suite of trace elements - collaboration among Gills, Kramer, Berman, Mee and Morita.

2. Prepare GESREM 2 as a research material, with recommended values for organo-chlorine pesticides, chlorobiphenyl congeners, PAHs and toxic trace elements - collaboration among Gills, Mee, Dawson, Boyd, Wade and Kramer.

3. Complete workbook on proper use of standards and reference materials - (Wade) with views and suggestions from Berman, Winter, Morita, Walton, Ridout and Yu Guohui.

4. Reprint and distribute the latest revision to the reference material catalogue - Ibe, Mee.

B. Possible New Actions

1. As a result of the discussion on the previous agenda items, GESREM identified a set of high priority needs for new reference materials.

87 For each of these, there are activities that GESREM could undertake to promote the preparation of these reference materials. Definition of these activities require careful thought and consultation with appropriate colleagues. It was decided that a small team would be created to work by correspondence and develop a specific task designation as proposed for each of these high priority needs. Dr. Gills suggested an outline (Annex VI) for these proposals. The proposals will be prepared by 1 December 1992 and will be incorporated in the GESREM workplan for 1994-1997.

88 These high priority needs are (not in priority order):

(i) inorganic nutrients in seawater - Berman, Aminot, Winter, Ridout
(ii) algal pigments - Dawson, Gills, Winter
(iii) algal toxins - Boyd, Dawson
(iv) CO_2/alkalinity in seawater - Dickson, Ridout, Gills
(v) "non persistent" pesticides in sediments - Dawson, Knap, Mee
(vi) dissolved organic carbon and nitrogen in seawater - Knap

2. A key recommendation of GESREM II in Halifax in 1990 was that GESREM should acquire and send free of charge reference materials to developing countries to promote the use of standards and reference materials and to encourage the participation of recipients in intercalibration exercises as part of the effort to improve the quality and intercomparability of data obtained from marine pollution studies in these regions. Dr. Calder wondered if the Group still believes that this was an important undertaking.

89 The Technical Secretary remarked that to a certain extent this was already in progress in several regions in the context of regional pollution monitoring and control programmes which IOC is co-sponsoring with UNEP and other Agencies. He said that reference materials had been provided by MESL, IAEA, Monaco who had also been supervising the intercalibration exercises that have been carried out under the aegis of GEMSI, and that already some form of networking has been established. There was considerable experience upon which GESREM could build and bring the recommendation in this regard set in Halifax in 1990 to fruition. The Group agreed that any effort in respect of the distribution of reference materials and intercalibration exercises should be a collaborative effort between GEMSI and GESREM. The availability of GESREM-2 will provide an opportunity for action that will be overseen by the IAEA.

3. It is the recommendation of the task sub-group that a large lot of highly contaminated mussel be procured for use as GESREM 3. The lot size should be a minimum of 1,000 30g freeze-dried weight units (30 kg total). Efforts to obtain this material will be co-ordinated through IAEA, NRC, NIES, NIST, and the University of Maryland. The following milestones are anticipated during the coming months:

December 1992	-	search and selection of sampling site or source for the highly contaminated mussels
February/March 1993	-	collection/procurement and processing of candidate material
June/May 1993	-	final processing and bottling.

90 It is anticipated that the above time table may change according to the availability of funds and source of base material.

7.2 PREPARATION OF DRAFT WORK PLAN FOR SUBMISSION TO SPONSORING AGENCIES

91 The Vice-Chairman agreed to prepare the GESREM workplan for 1994-1997 and submit it for consideration by GIPME and the IOC. The workplan will be based on input from individuals identified in Agenda Item 6.1, and will be ready for submission by 1 January 1993.

7.3 ROLE OF GESREM VIS-A-VIS OTHER IOC EXPERT GROUPS

92 It is becoming increasingly clear that the roles of the three GIPME expert groups (GESREM, GEMSI, GEEP) are interdependent and require frequent interaction. For example, GEMSI will soon produce a report defining the most serious contamination problems in each region of the world. This will provide a guide to GESREM for reference material requirements in each of these regions. Also, the GEEP-GEMSI workshop in Mazatlan will identify modern pesticides that are persistent in the environment and that cause biological effects. This will provide a justification for GESREM to provide appropriate reference materials.

93 Occasionally, confusion exists concerning the roles of GESREM and GEMSI because of the similarities in titles.

94 In response to the statement of the Chairman of the Committee for GIPME under Agenda Item 1, the chairmen of both GESREM and GEMSI agreed to prepare a statement that define the roles and interactions of the two groups, as follows.

95 The role of GESREM focuses on improving the availability of certified reference materials for marine environmental science. This is a unique role, not covered by any other UN sponsored group. The membership of GESREM includes not only experts from the marine science community but most importantly representatives from the major global producers of reference materials. While GEMSI had originally intended to cover this area, its other goals, i.e. improving analytical methodology and improving comparability of measurements among laboratories, required their full attention. Thus the need for another group, GESREM, to provide a mechanism for fulfilling the requirements for reference materials.

96 The two groups are very complementary and have strong interactions at the present time. These interactions are expected to strengthen in the future, especially as GEMSI (and GEEP) identify new chemicals of environmental significance for which reference materials will be required. New thrusts already identified include "non-persistent" pesticides, algal toxins, and materials to support JGOFS and WOCE studies over the next 5 years. GEMSI and GEEP will be expected to determine the priorities for reference materials, while GESREM will determine the feasibility of preparing the materials, promote their actual production, and co-ordinate the distribution of reference materials on a global basis. GESREM also has a mandate from GIPME to provide guidance and training on the proper use of reference materials as part of an overall quality assurance/quality control programme.

8. GESREM THE GROUP

8.1 REVIEW OF GESREM MEMBERSHIP

97 The Meeting reviewed the present membership of GESREM and agreed that it represented an excellent cross-section of the most important producers of reference materials/certified reference materials/standard reference materials, as well as users of reference materials. The Chairman noted the participation of an expert from the major producer of marine reference materials from China as a positive development for the growth of GESREM. The Meeting requested the Secretariat to include an expert from the Laboratory of the Government Chemist (U.K.) and one expert each from Russia and Eastern Europe. The Group would also benefit from the inclusion of a marine biologist with an interest in reference materials.

8.2 ELECTION OF OFFICERS FOR THE NEXT INTERSESSIONAL PERIOD

98 The present Chairman announced that he would be standing down after a most rewarding time in office and thanked the members and the joint sponsors of GESREM for the support given to him. The Technical Secretary, on behalf of the joint sponsors of GESREM expressed satisfaction at the progress made by GESREM under the leadership of Dr. Jamieson and requested that he continue to be associated with the Group in some ex-officio capacity.

99 Dr. John Calder who had been Vice-Chairman of GESREM in the last intersessional period was elected Chairman for the next intersessional period while Dr. Alan Walton, Director of the Oceanographic Centre, Rimouski, Québec and former director of the IAEA laboratory, Monaco was elected Vice Chairman, all by acclamation.

9. PLACE AND DATE OF NEXT MEETING

100 The Meeting agreed to hold the next Meeting (GESREM IV) toward the end of 1994 at a location yet to be confirmed.

10. ADOPTION OF THE DRAFT SUMMARY REPORT

101 The Draft Summary Report was considered by the Group and adopted with minor amendments.

11. CLOSING

102 The Chairman, Dr. Jamieson thanked the participants for a very productive Meeting. The Technical Secretary of IOC, on behalf of the sponsors and participants expressed profound appreciation to the Management Unit for the North Sea Mathematical Models of the Belgian Ministry of Public Health and Environment for being such wonderful hosts.

103 The Chairman closed the Meeting by 12:30 p.m. on Thursday, 24 September 1992.

ANNEX I

AGENDA

1. OPENING OF THE SESSION

2. ADMINISTRATIVE ARRANGEMENTS

2.1 ADOPTION OF AGENDA
2.2 DESIGNATION OF RAPPORTEUR
2.3 CONDUCT OF THE SESSION

3. STATUS OF ON-GOING GESREM ACTIVITIES

3.1 PREPARATION OF REFERENCE MATERIALS GESREM 1 AND GESREM 2

3.1.1 GESREM 1
3.1.2 GESREM 2

3.2 FINAL DRAFT OF THE SECOND UPDATE TO THE REFERENCE MATERIAL CATALOGUE
3.3 WORK BOOK ON THE PROPER USE OF STANDARDS AND REFERENCE MATERIALS

4. THE COMMUNITY BUREAU OF REFERENCE (BCR)

5. REVIEW OF STATUS AND NEEDS FOR NEW REFERENCE MATERIALS

5.1 INORGANIC NUTRIENTS IN SEAWATER
5.2 THIOSULFATE FOR WINKLER TITRATIONS
5.3 PIGMENTS AND ALGAL CULTURES
5.4 ALGAL TOXINS
5.5 CARBON DIOXIDE IN SEAWATER
5.6 NON-PERSISTENT PESTICIDES IN NATURAL MATRICES
5.7 SEDIMENT ANCILLARY PARAMETERS
5.8 METABOLITES OF PAHs
5.9 METHYL MERCURY COMPOUNDS
5.10 ICP - MS TRACE ELEMENT STANDARDS
5.11 PLANAR POLYCHLORINATED BIPHENYLS
5.12 DISSOLVED ORGANIC CARBON (DOC)

6. NEEDS IDENTIFIED BY OTHER GROUPS

6.1 IOC GROUP OF EXPERTS ON METHODS, STANDARDS AND INTERCALIBRATION (GEMSI), IOC GROUP OF EXPERTS ON THE EFFECTS OF POLLUTION (GEEP)
6.2 UNITED NATIONS ENVIRONMENT PROGRAMME (UNEP)
6.3 INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA)

6.3.1 Review of Intercalibration Exercises Organized by MESL on Behalf of IOC, IAEA & UNEP (since 1990)

6.4 INTERNATIONAL COUNCIL FOR THE EXPLORATION OF THE SEA (ICES)
6.5 JGOFS, WOCE, GLOBEC, INTERNATIONAL PROGRAMMES

7. GESREM WORK PLAN FOR 1993-1997

7.1 ACTION ITEMS AND MEMBERS RESPONSIBLE FOR THEIR IMPLEMENTATION
7.2 PREPARATION OF DRAFT WORK PLAN FOR SUBMISSION TO SPONSORING AGENCIES
7.3 ROLE OF GESREM VIS-A-VIS OTHER IOC EXPERT GROUPS

8. GESREM THE GROUP

8.1 REVIEW OF GESREM MEMBERSHIP
8.2 ELECTION OF OFFICERS FOR THE NEXT INTERSESSIONAL PERIOD

9. PLACE AND DATE OF NEXT MEETING

10. ADOPTION OF THE DRAFT SUMMARY REPORT

11. CLOSING

RECOMMENDATIONS

Recommendation GESREM - III.1

PREPARATION OF A CERTIFIED REFERENCE MATERIAL FOR ORGANO-CHLORINES IN MUSSEL TISSUE

The Group of Experts on Standards and Reference Materials (GESREM),

Noting that the International Mussel Watch and national and regional monitoring programmes require such a material,

Considering that the existing material, GESREM-2, has insufficient mass to serve as a universally available reference material,

Recommends that the sponsoring agencies provide the necessary support for collection and preparation of a new mussel material of sufficient mass to be called GESREM-3, that will become a certified reference material.

Recommendation GESREM - III.2

MEMBERSHIP OF GESREM

The Group of Experts on Standards and Reference Materials (GESREM),

Noting that its effectiveness depends in part on participation by all significant suppliers of reference materials for marine science,

Recommends that the sponsoring agencies invite to membership in GESREM a representative of the Laboratory of the Government Chemist (U.K.) and seek out organizations in Russia and Eastern Europe that also should participate.

Recommendation GESREM-III.3

ADDITIONAL INFORMATION ABOUT REFERENCE MATERIAL

The Group of Experts on Standards and Reference Materials (GESREM),

Noting that the value of reference materials is directly related to the amount of information supplied by the producers, and

Noting further that with some additional effort the value of many reference materials could be enhanced,

Recommends that whenever feasible, documentation of sediment-based reference materials report information on particle size distribution, that reference materials for chlorobiphenyl congeners report certified values for as many as possible of the co-planar congeners, and that reference materials certified for total mercury also have certified or information values for methyl-mercury.

ANNEX III

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ANNEX IV

PRESENT AND FUTURE PLANS OF REFERENCE PRODUCERS

Standards and Reference Material Developments in China

In the past 10 years or more, development has been made on marine environmental monitoring and study in China. Chinese marine scientists pay great attention to data quality. The need for standards and reference materials in the marine community has been recognized gradually. In China, there is a National Research Centre for Standard and Reference Materials in Beijing. This Centre is responsible for producing and providing different materials including the marine reference materials. China has 18,000 km of coast line, more than 6,000 islands, a vast marginal sea and very wide continental shelves. In the coastal zones of the whole country, marine management offices and monitoring networks have been set up. For these and other reasons, it is desirable to develop and maintain a wide variety of standards and reference materials.

In China, at the Second Institute of Oceanography of the State Oceanic Administration located in Hangzhou, a Marine Standard Materials Centre was established in 1988. We have a number of specialized researchers engaged in the study and production of the standard materials. At present, the main products are:

1. Synthetic standard solutions for nutrients. These are very similar to the Japanese CSK Standards. An intercalibration with the Japanese scientists in the China-Japan co-operative investigation was also carried out. The series of nutrients standard solutions includes ammonia, nitrate, nitrite, phosphate, silicate and hydrochloride acid and potassium iodate, etc.

2. Trace metals in water and seawater (mainly coastal waters) including Cu, Pb, Zn, Cd, Cr and Hg, etc.

3. Mussel tissue. 21 elements, both major and trace components, but mainly inorganic were certified in samples collected from coastal zones in China.

4. Sediment Standard Materials. Certified for 60 elements.

5. Six kinds of rock and mineral reference materials were produced by the Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources. They are used in the analysis of marine sediment on occasion.

6. An open ocean sediment standard material with special attention given to manganese nodule standards for use in the Chinese Multimetal-nodule exploration in the Northwest Pacific Ocean has just been prepared.

7. All of these standards and reference materials are commercially available in China at a relatively low cost.

Future considerations for marine standards and reference materials are:

1. For the best guarantee of high quality comparable data, the employment of reference materials should be widely accepted by the marine scientific community.

2. The production, certification and distribution of the standards and reference materials should be better arranged. The reduction of cost for the materials is also important.

3. New materials are required. The priority for standards and reference materials should be put on nutrients and series of organic pollutants especially different compounds in oils, speciation of metals, etc.

COMMISSION OF THE EUROPEAN COMMUNITIES - JOINT RESEARCH CENTRE

Preparation of Biological and Environmental Reference Samples and Materials at the Central Bureau for Nuclear Measurements.

CBNM has established a unique facility for the preparation of biological and environmental reference samples and materials. The aim of this facility is the preparation of materials in amounts of typically 50 to 200 kg fresh material, processed to 5 to 20 kg dry powder. It includes a technology hall equipped with a 8 m^2 laminar flow cell, a specially developed freeze-drier with a shelf surface area of 5.4 m^2, special Teflon cryo-grinding equipment and advanced milling equipment.

A versatile system of glove boxes allows handling (sieving, mixing, bottling) under controlled atmospheric conditions. Production control equipment for humidity, particle size and trace metal analysis is available on site.

This facility is used for the production of Certified Reference Materials (CRM's) on behalf of the Community Bureau of Reference (BCR) and also for the production of customer tailored reference materials and samples for round-robins, quality control testing, etc.

Examples of reference samples and reference materials prepared by CBNM

- cod fish powder candidate CRM for trace elements;
- orange juice powder for the certification of amino-acids, sugars, vitamins;
- several milk powder CRMs and round-robin samples;
- paprika and lettuce powder for the analysis of trace elements;
- plastic CRMs for the analysis for traces of cadmium;
- pig liver powder round-robin samples for the analysis of trace elements;
- several sediments for organo-metallic analysis;
- fly ash for the analysis of dioxins.

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IAPSO STANDARD SEAWATER SERVICE

1. The IAPSO Standard Seawater Service continues to be operated by Ocean Scientific International Ltd. (OSIL) which is based at Wormley in Surrey, U.K.

2. Dr. Fred Culkin remains with the company as a consultant analyst and an additional chemist has been employed and fully trained in all aspects of the calibration.

3. Sales of ampoules remain at the annual average of 11,500. Global programmes such as WOCE and JGOFS have shown no significant increases in demand to date. The standard is currently used in over 65 countries.

4. Ampoule label information has been changed. The chlorinity value has been replaced by salinity as this is more appropriate to modern applications. The conductivity ratio K_{15} remains as the main calibration value on the label.

5. A new standard with a salinity of 38 was introduced during 1991 to provide an additional calibration point for measurements above 35. The full range of Standard Seawaters comprises salinities of 10, 30, 35 and 38 with the 35 salinity, Normal Standard Seawater, remaining as the main calibration point.

6. The company has successfully carried out a number of training courses for personnel in Europe, on the correct procedure for measuring salinity in the laboratory. In order to provide training material for developing countries the production of a video is under consideration.

7. During Spring 1995, the Institute of Oceanographic Sciences Deacon Laboratory (IOSDL), who rent the current Standard Seawater accommodation to OSIL, will move to a new purpose-built facility in Southampton. OSIL are presently investigating options with regard to their accommodation at that time.

Low-nutrient seawater

OSIL have developed a natural oceanic seawater with minimal levels of nutrients for use as a blank and in the preparation of standards for high precision nutrient analysis. A real seawater matrix is essential for many of the modern analytical methods. Low Nutrient Seawater (LNS) is available in 1 litre bottles and carries analysis data for the major nutrient levels. Typical values are as follows:

Phosphate < 0.05uM, Nitrate < 0.1uM, Nitrite < 0.05uM, Silicate < 1uM.

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QUALITY ASSURANCE PROJECT OF THE NOAA NATIONAL STATUS AND TRENDS PROGRAME

The Quality Assurance (QA) Project of the NOAA National Status and Trends (NS & T) Programme conducts annual intercomparison exercises as part of its activities. The trace metal intercomparison exercises are organized by the National Research Council of Canada, and trace organic exercises by the National Institute of Standards and Technology. Exercise sample matrices vary from year to year to meet NS & T analysts needs. Participation in these exercises on a voluntary basis by non-profit laboratories has increased since the inception of the QA Project and will continue to be encouraged as funds permit.

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USEPA Reference Materials Programme

In 1991, USEPA's Chemical Reference Materials Programme was transferred to five selected commercial suppliers under co-operative research and development agreements to permit their sale as "EPA certified" materials, after verification and approval by EPA. EPA's biological and microbiological reference materials and chemical materials of lower demand (orphan compounds) are still available for free from EMSL-Cincinnati.

There is a renewed interest in reference materials such as plant and animal tissues, aquatic plant pigments, nutrients, sediments, etc. for EPA's expanded estuarine and marine monitoring activities.

The USEPA has a great interest in relaxing the method requirements for monitoring and regulation, in order to allow more easily other analytical methods to be used if they meet a prescribed set of performance criteria.

However, there is a realization that this approach must consider the following :

- an initial and continuing demonstration of method performance, following a prescribed protocol.
- a reference method for each analyte
- increased requirements for QA/QC checks
- increased participation in interlaboratory performance evaluation studies
- increased oversight by regulating authorities.

NATIONAL RESEARCH COUNCIL, CANADA
MARINE ANALYTICAL CHEMISTRY STANDARDS PROGRAMME

A. Institute for Marine Biosciences, Halifax

Current activities underway at NRC can be described under the following categories:

1. PAHs

a) well advanced on 2 instrument calibration solutions of perdeutero compounds:
DPAC - 1, 21 compounds, for GC-MS
DPAC - 2, 6 compounds, for LC-fluorescence

b) Re-certification of marine sediments HS3 - HS6. We intend to tighten the uncertainty limits but problems have been encountered.

Supercritical Fluid Extraction (SFE) shows that Soxhlet extraction does not recover all of the PAHs.

At NRC it has been found that traditional Soxhlet extraction of marine sediments for PAH analysis yields data of excellent precision, and that 48 hours extraction time gets everything out that will come out. However, SFE with n-pentane gave different results. For example, the sediment residue <u>following</u> Soxhlet extraction was subjected to SFE, and additional quantities of PAHs were thus extracted. These additional quantities varied from case to case, but the average value was 20% or so (a <u>systematic</u> discrepancy). Similar experiments on NIST materials (urban dust, SRM 1649, and diesel particulates, SRM 1650) gave a less marked discrepancy. Presumably this reflects the larger and more variable particle size in the sediments, for which the penetrating power of the supercritical fluid made a large difference. Of course, one could ask the question as to which is the "correct" answer. If Soxhlet extraction can not access this extra 20%, is this material a bio-hazard? Is this a case for "method-specific certification", or should we remove the certification and issue as an uncertified material?

2. PCBs - we have started re-certification of HS-1 and HS-2 and hope to tighten uncertainties <u>and</u> extend to more congeners.

3. Marine Toxins

a) Domoic acid - amnesic shellfish poisons (ASP)

- existing DACS - 1, solution of pure compound in water/acetonitrite - stability seems okay, stocks becoming depleted.

- MUS-1 (mussel tissue homogenate) - a problem has been identified. The material was originally certified at 126 ± 1µg/g, now 2 1/2 years later is at 98 ± 5 µg/g. Material was stored in an air-conditioned room, now in a 4°C refrigerator. Freezing is dangerous, since separations occur which on thawing cause local concentration increases in solution components. These appear to induce decomposition of the labile toxins. This material shows signs of depletion as a result of the major ASP incident on the U.S. West Coast in 1991.

b) Paralytic shellfish poisons (PSPs)

We have available purified samples of the 3 PSP toxins which are most important in shellfish from the North Atlantic coasts of North America. We will release standard solutions of these, probably in 1993, but the documentation will have to contain a *caveat* concerning long-term stability. Also, it is not possible to weigh these materials accurately, as they are extremely hygroscopic and very difficult to produce entirely free from salts. Quantitation will involve integration of appropriate NMR signals relative to those from a (weighable) internal standard, probably arginine.

We have also completed stability studies on tissue slurry materials from scallop liver and roe. The liver looks promising, and we shall probably release a material of some kind, but it is unlikely that this will ever be a "certified reference material".

c) Diarrhetic Shellfish Poisons (DSPs).

The best-known members are okadaic acid, and its methyl homologue DTX-1, but NRC has discovered several new members of the DSP family.

We have almost completed a stability study of pure okadaic acid in solution, and hope to release an instrument calibration solution in 1993.

We are also trying to establish a mussel tissue slurry reference material for DSPs. Work is going well so far, and it might be possible to release a material of some kind (with appropriate *caveats*) in late 1993 or 1994.

B. Institute for Environmental Chemistry, Ottawa

1. An activity has been recently initiated regarding the feasibility of preparing a CRM for nutrients in seawater. The major problem is to ensure the stability of the sample for a long enough period of time so that the reference material will be of use. We will expand on the work of Alain Aminot (IFREMER). With the co-operation of the Bedford Institute of Oceanography, we have begun a series of stability experiments using various approaches other than autoclaving in order to obviate the use of glass containers which would preclude the certification for silica.

2. A feasibility study regarding the preparation of a fish tissue certified for dioxins, furans and other pertinent organochlorines and pesticides has been successfully concluded. We are now in the process of certifying a fish tissue prepared as a stabilized slurry. We expect the material to be in distribution within the next year.

3. We are evaluating the possibility of producing a CRM for mercury in seawater. The problem is the inherently low concentration (< 1ng/L) and whether we can certify at this level without too large uncertainties.

NATIONAL INSTITUTE FOR STANDARDS AND TECHNOLOGY (NIST)

Several NIST Standard Reference Materials (SRMS) were completed or initiated during 1992 in the areas of marine and/or environmental science. Most are renewals but a number are being made available by NIST for the first time. A brief description of these materials is given below.

Geological and Ores

1)	SRM 2109 San Joaquin Soil	25-30 elements (base line levels)
2)	SRM 2710 Montana I Soil	25-30 elements (highly contaminated)
3)	SRM 2711 Montana II Soil	25-30 elements (moderately contaminated)
4)	SRM 1941a River Sediment	Trace Organics (PAHs, PCBs, etc.)
5)	SRM 1946a Estuarine Sediment	30 - 40 elements
6)	Denver Sewage Sludge (Domestic)	15 - 20 elements
7)	New Jersey Sewage Sludge (Industrial)	15 - 20 elements
8)	Diesel on Soil	Diesel Fuel

Marine Standards

9)	SRM 1941a Mussel Tissue	Selected PAHs, PCBs
10)	Whale Blubber	Selected PAHs, PCBs

Food and Nutrition

11)	Nutrients in Infant Formula	Nutrients, Vitamins
12)	Caratenoids in Foods	Pure forms

Pesticides

RM 8464	Aldrin	purity
RM 8465	Dieldrin	purity
RM 8466	α-HCH (Lindane)	purity
RM 8467	4,4'-DDE	purity
RM 8468	Heptachlor	purity
RM 8469	4,4'-DDE	purity

NATIONAL INSTITUTE OF ENVIRONMENTAL STUDIES (NIES) JAPAN

In the past 14 years, the National Institute of Environmental Studies (NIES), Japan, has produced certified reference materials (CRMs) which are important in the quality assurance and development of methods in environmental analysis. In the first period (1978-1990), ten CRMs including freeze-dried mussel and sargasso weed as marine CRM were prepared and certified values given for the concentrations of various elements.

In the second period starting in 1991, a new generation CRM is being considered which defines the chemical speciation of a number of elements. The first choice of elements was tin, mercury and arsenic all of which change in chemical form in the marine environment.

NIES No. 11. Fish Tissue was prepared by freeze-drying sea bass collected in Tokyo Bay. The material is certified for tributyltin and total tin concentration and is being distributed with information for triphenyl tin. Most of the tin present in the material is in the form of organic-tin.

NIES No. 12. Marine Sediment is also for tin speciation. The material was prepared from the sediment in Tokyo bay and will be distributed in 1993 with certified values for total tin and organic tin concentrations in addition to information on elemental composition.

NIES No. 13. Human Hair is being prepared for mercury speciation. Human Hair is powdered at liquid nitrogen temperature. We are currently in the process of analysis. Because Japanese eat significant amounts of marine-derived food, the concentration of mercury in hair is about 3 ppm, being mostly in the form of methylmercury.

NIES No. 14 and No. 15. CRMs will be marine biological materials certified for arsenic species. Candidates are clam, mussel, oyster, squid, and macroalgae which are now being examined for their feasibility. Other elements considered for chemical speciation CRMs in the future include Se, Cd, Cr, Co, Ni, Pb and I.

NIES is also considering organic pollutants such as dioxins and furans, PCBs, PAHs in biological and environmental materials.

ANNEX V

GLOSSARY OF TERMS (REVISED)

Reference Material (RM) : A material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

Certified Reference Material (CRM) : A reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

Standard Reference Materials (SRMs) : Certified reference materials issued by NIST (National Institute of Standards and Technology).

Instrument Performance Standard : A synthetic material of known purity prepared for the calibration of instruments or intercomparison of measurements.

Accuracy, Precision and Bias : Historically, the term precision, has been used to describe the variability of measurements and the term, accuracy, to describe the closeness of measurements to true values. However, in recent years, statisticians have begun using a more specific term, bias, to describe the closeness of measurements to true values.

ANNEX VI

PROPOSALS FOR NEW REFERENCE MATERIALS

To provide guidance for GESREM in establishing priorities, strategies and milestones and identifying resources for Reference Materials in Marine Science, a formalized proposal is needed. Such a proposal will enhance the probability of achieving the goals and objectives of GESREM and would ensure that project focus is maintained. An outline is given below as a suggested outline for proposal submissions. The outline is given with the understanding that GESREM will entertain only proposals that respond to real technical needs and problems.

1. Project Description/Title

2. Justification

3. Project Goals (project deliverables to address needs)

4. Approach (describe measurements or studies needed to achieve goals)

5. Background (what information is available, sources, consultants)
   References (available standards).

6. Resources
   Materials
   Analytical

7. Accuracy Requirements
   Precision Requirements

8. Alternative Approaches/Substitutes

9. **Project Rating Criteria**

Project Rating Criteria	Suggested Max. Available Points
GESREM Mission	20
Degree of National Concern	30
Available Resources	30
Ongoing Standards Activity	10
Technical Champion (available)	10