Intergovernmental Oceanographic Commission Reports of Meetings of Experts and Equivalent Bodies



IOC-UNEP Group of Experts on Methods, Standards and Intercalibration

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Seventh Session

Monaco, 13-20 November 1985

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IOC-UNEP Group of Experts on Methods, Standards and Intercalibration

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In this Series

Reports of Meetings of Experts and Equivalent Bodies, which was initiated in 1994, the reports of the following meetings have already been issued:

- Third Meeting of the Central Editorial Board for the Geological/ Geophysical Atlases of the Atlantic and Pacific Oceans
- Fourth Meeting of the Central Editorial Board for the Geological/ Geophysical Atlases of the Atlantic and Pacific Oceans
- Fourth Session of the Joint IOC-WMO-CPPS Working Group on the investigations of «El Niño»
- First Session of the IOC-FAO Guilding Group of Experts on the Programme of Ocean Science in relation to Living Resources
- First Session of the IOC-UN(OETB) Guiding Group of Experts on the Programme of Ocean Science in relation to Non-Living Resources
- First Session of the Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets
- First Session of the Joint CCOP (SOPAC)-IOC Working Group on South Pacific Tectonics and Resources
- First Session of the IODE Group of Experts on Marine Information Management
- Tenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies in East Asian Testonics and Resources
- Sixth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration
- First Session of the IOC Consultative Group on Ocean Mapping
- Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ships-of-Opportunity Programmes
- Second Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources
- Third Session of the Group of Experts on Format Development of the Working Committee on International Oceanographic Data Exchange
- Eleventh Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of South-East Asian Tectonics and Resources
- Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets

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1. OPENING OF THE SESSION

The Chairman of GEMSI, Dr Jan C. Duinker, opened the meeting at 10.00 hours on 13 November 1985 by welcoming the members to the Seventh Session of the Group. (A list of participants is given in Annex III). He thanked the host of the Session, Dr. Rinosuki Fukai, the Director of the International Laboratory of Marine Radioactivity, (Musée Océanographique Monaco) for having kindly offered to accomodate the meeting and for all the preparations he had undertaken. He expressed his regrets that the UNEP Technical Secretary, Dr Simon Aston, had been ill for some time and would be unable to attend the session; he suggested that the Group send a telegram wishing Dr Aston a speedy recovery.

Dr Fukai responded by welcoming the participants on behalf of the Director General of the IAEA and indicated that he was particularly pleased that GEMSI was meeting in the Monaco Laboratory since staff of the laboratory have been involved with the work of GEMSI since the Group's inception and that the laboratory's association with the Group had been further strengthened since the co-sponsoring of GEM' by UNEP and the increased role of the laboratory in UNEP programmes. The collaboration with GEMSI is anticipated to continue through the involvement of the next Director, and GEMSI member, Dr Alan Walton.

The Chairman informed the Group of the very full agenda before it and indicated that an attempt had been made, to make this Agenda operational in character, and that it was the Group's responsibility to the Working Committee for GIPME and the GIPME Programme to supply sound advice to the Secretariat of IOC, which is at present understaffed, due to the limited resources in UNESCO and the movement of staff members. He invited the Chairman of the Working Committee for GIPME, Dr Neil Andersen, to address the Group.

Dr Andersen informed the Group that the Thirteenth Session of the IOC Assembly had favourably received the reports of the work of GEMSI. He was particularly pleased with the rapidity with which GEMSI had responded to the issue of the availability of Standards and Reference Materials and he perceived considerable progress in this area of the GIPME Programme.

He expressed the nope that this meeting would provide a report of progress for the next IOC Executive Council Meeting and indicated that a meeting of the Officers and Secretariat of the GIPME Programme had recently completed a fairly comprehensive appraisal of the programme.

He expressed his concern with regard to the resources, both financial and manpower, available to the IOC, and suressed that GEMSI should be careful in broadening its horizons at this stage and should be realistic about priorities. He also mentioned that the Group of Experts on the Effects of Pollutants (GEEP) was now making considerable progress and is also drawing on the limited resources available to the IOC.

He pointed out that the IOC had succeeded in filling the position of the Head of the Marine Pollution Research and Monitoring Unit with an extremely competent and energetic individual, in the person of Dr Gunnar Kullenberg. He pointed out, however, that for the immediate future, Dr Kullenberg will be the only person in the Unit. As a result, Dr Andersen called upon all members of GEMSI to continue their present strong assistance to the Secretariat, and whenever possible, to increase these efforts. He cautioned, however, that this should not be misunderstood as being a longterm solution to the manpower problem.

The Chairman referred to the transfer of the Ocean and Coastal Areas Programme Activity Centre of UNEP and indicated that current problems in the process of recruiting new staff for the programme have caused some delays in activities, but that good cooperation between the IOC and UNEP exists and he had every expectation that their collaboration would be strengthened, especially in the work of GEMSI.

2. <u>ADMINISTRATIVE ARRANGEMENTS</u>

2.1 ADOPTION OF THE AGENDA

The Group adopted the Agenda (Annex I) without amendments.

2.2 DESIGNATION OF RAPPORTEURS

The Chairman adopted the suggestion made by the IOC Secretariat in earlier communications that individuals be assigned to the reporting of specific Agenda Items. These would be, for the most part, based on the reporting responsibility of the various <u>ad hoc</u> Group Chairmen to introduce items.

2.3 CONDUCT OF THE SESSION

The IOC Technical Secretary, Dr Rodger Dawson, introduced the documentation available at the Session. He commended the <u>ad hoc</u> Group Chairmen on their cooperation in preparing the majority of the reports well in advance of the Session. Only a few reports were unfinished and he asked for the Group's indulgence, while these were finalized at the Session. Information documents provided by IOC, UNEP and IAEA were available for consultation as appropriate.

The Group would normally work in plenary, but arrangements could be made at the discretion of the Chairman for work in sessional sub-groups and these would be announced as they were established.

3. <u>INTERSESSIONAL ACTIVITIES</u>

3.1 THE ANALYSIS OF INDIVIDUAL ORGANIC CONTAMINANTS

Substituting for Dr Kathy Burns, Chairperson of the <u>ad hoc</u> GEMSI Sub-Group on Individual Contaminants, but unable to attend the meeting, Dr Manfred Ehrhardt reported on intersessional activities. The Group had met at the Insti⁺ut für Meereskunde in Kiel, Federal Republic of Germany, in June 1985. At the meeting, the following topics were discussed:

- evaluation of the PANCAL 1984 Workshop at the Bermuda Biological Station for Research (1-15 December, 1984) and recommended changes on analytical methods for dissolved/dispersed hydrocarbons (Manuels and Guides Nº 13);
- methods for the analysis of chlorinated hydrocarobons.
 Revision of Reference Method Nº 14 and of techniques to include capillary gas chromatography;
- plans for incorporating organic contaminants in the open ocean baseline programme;
- progress on sampling and analysis of individual organic contaminants related to:
 - (i) atmospheric deposition
 - (ii) reaction products generated in the environment
 - (iii) high fat samples and polar contaminants
 - (iv) riverine fluxes
 - (v) seawater analysis
- strategies for the use of sediments to monitor organic contaminants;
- outline for a book chapter on the analysis of PCBs in seawater.

The report of the sub-group meeting in Kiel is presented in Annex IV. In the discussion following Dr Ehrhardt's presentation, Dr Duinker confirmed that for the purpose of characterizing and quantifying individual chlorinated hydrocarbons, reference compounds could, in principle, be synthesized in Kiel in sufficient quantity. Restrictions are the availability of manpower, insufficient purity of precursor Compounds for synthesis and difficulties in separating, on a preparative scale, pure compounds from other reaction products. It was recognized that not all reference compounds would be the same for atmospheric samples, water samples, particles and tissue. Parallel developments within ICES were mentioned, but Dr. Dawson assured that duplication would be avoided through cooperation between ICES and IOC. This subject will be discussed during the forthcoming meeting of the MCWG of ICES in February 1986. It was noted that caution should be exercized concerning the composition of reference materials. Difficulties are expected in preventing compositional changes of lipophilic material concentrated from seawater.

With respect to the reporting of analytical results, it was stressed that authors should, especially in the case of chlorinated hydrocarbons, include chromatograms in their publications to facilitate comparison and evaluation.

Atmospheric contaminants can be assessed with respect to their concentrations in different matrices (e.g. vapour phase, rain, particles), but the measurement of atmospheric deposition velocities is beyond present analytical capabilities. Difficulties were mentioned regarding artefacts resulting from the sampling method (eg. exchange of contaminants between vapour phase and particles, when both phases are not in equilibrium concerning specific contaminants). There seems to be no immediate solution to this problem.

3.2 USE OF MARINE SEDIMENTS IN MARPOLMON

Dr Schink presented a draft of the "Guidelines for the Design and Conduct of a Programme to Assess Contamination in Marine Sediments". This document was prepared in large part by an <u>ad hoc</u> working group that met in Kiel, FRG, 10-19 June 1985. Material developed by the Group has since been edited and revised on the basis of comments received. GEMSI discussed this draft document and concluded that guidelines are necessary, but difficult to prepare. GEMSI agreed that this would be a useful document but substantial questions concerning the actual form were raised. It was recommended that the IOC Secretariat and the Officers of the Programme consider this, and suggest a future course to follow with respect to the issuance of guidelines.

3.3 THE USE OF MARINE ORGANISMS IN MARPOLMON (Musselwatch)

Dr. Graham Topping informed the Group that following the Sixth Session of GEMSI, he had been asked by the IOC to expand on the work proposals regarding the review of musselwatch activities. Subsequently, UNEP and IOC had approached him to prepare and distribute a questionniare to selected people in the various regional programmes of IOC and UNEP. A draft questionnaire was distributed to the Group for comment and amendment, and a revised version was to be prepared at a sessional sub-group (see Annex V).

Following these deliberations, Dr Topping informed the Group that he would be sending the final version of the questionnaire to IOC for distribution in January 1986. He hoped to produce an inventory of Musselwatch activities and a preliminary assessment of the quality of data being collected for the next Session of the WC/GIPME. A more detailed assessment of these data and the consideration and production of guidelines for a Global Musselwatch would have to be done by the GEMSI <u>ad hoc</u> Group on Marine Organisms.

3.4 RIVER INPUTS OF POLLUTANTS TO THE COASTAL ENVIRONMENT

During the meeting of GEMSI VI in Woods Hole, the sub-group prepared a questionnaire to be circulated to potential participants of the proposed River Input of Pollutants Intercalibration Exercise, so that their comments, interests and experiences could be taken into account when formulating the final workshop design. This questionnaire was sent out by the Chairman of the sub-group, Dr Herbert Windom, during December 1984.

The sub-group Chairman met with a local steering committee for the proposed exercize in Thailand during January 1985, while he was there to participate in a cooperative research programme. The purpose of this meeting was to discuss various logistical aspects of the proposed exercise with cooperating agencies in Thailand (see Annex VI). Dr Manuwadi Hungspreugs acts as Chairperson for this group and also provides overall liaison for GEMSI in Thailand.

Finally, five members of the sub-group met in Bangkok from 22 to 26 April 1985, to develop detailed plans for the exercise incorporating results of the questionnaire. The Group was chosen to give balance to both the organic and inorganic aspects of the design and logistics of the exercise.

From the responses to questionnaires sent to key agencies, institutions and individuals, it appears that participants from regional laboratories have some experience in river studies and are interested in participating in both inorganic (ie. trace metals) and organic aspects of the proposed exercise. For this reason, it is recommended that participation from regional laboratories be limited to about 12. Based on the responses to the questionnaires thus far, this number will probably allow for adequate regional participation. There will probably be six participating core laboratories.

The proposed exercise will be in the form of a workshop having the following three components:

- classroom discussions/demonstrations
- experiments
- intercalibration of analyses.

The first two components will provide the training part of the exercise. This will include classroom lectures and discussions on past experience with intercalibration exercises (eg. PANCAL), the basis and need for a river intercalibration exercise, general aspects of river transport pollutants (eg. hydrology, estuarine mixing, inhomogeneity, etc) and potential problems of sampling and analysis. Demonstrations of sampling and analytical techniques will be provided to give participants "hands on" experience. Participants will also be involved in experiments designed to address some fundamental problems associated with river transport studies.

For the intercalibration component, the participants will be involved in collecting and preparing samples to be returned to their home laboratories for pollutant analysis. Some analyses, however, will be performed during the workshop as well.

The sub-group met sessionally, to discuss the details of day-to-day activities during the proposed workshop. For this purpose, an organic and inorganic group met separately. The results of their deliberations were combined and will be included in a Workshop Prospectus by the sub-group's Chairman during the next two months and will be submitted to the IOC Secretariat. The Prospectus should then be sent to individual laboratories inviting them to participate.

During the sessional period, the sub-group also considered the cost of conducting the workshop and submitted proposals for consideration by the IOC and UNEP Secretariats.

3.5 THE AVAILABILITY OF STANDARDS AND REPERENCE MATERIALS

The Chairman of the sub-group, Dr Walton, reviewed the activities which had taken place since the group was formed, following the recommendations of GEMSI VI.

Two papers (IOC/GGE(MSI)-VII/12 and IOC/GGE(MSI-VII/13) present the discussions of (i) a preliminary meeting held in Geneva, 3-4 June 1985 and (ii) a larger gathering which included the producers of marine standard reference materials, held in Washington D.C, 28-30 October 1985. That meeting revealed a number of features of importance to the coordination of international efforts in this field, viz,

- (1) the present effort is substantial and is growing internationally;
- (ii) the producers, while familiar with each others work, do not meet to rationalize and coordinate their efforts on an international basis - consequently, overlapping efforts have developed;
- (iii) the principal producers are in Canada, the European Community (BCR), Japan (NIES), UK, USA (NBS, EPA, USGS and NOAA) and certain international organizations (IAEA and ICES);
- (iv) the marine science community throughout the world would benefit from being better informed as to the availability of material from all sources (NOAA offered direct assistance to any initiative in this area); and
 - (v) funding for the production of new reference materials remains limited, but most organizations are keenly conscious of the need and importance of the reference materials programmes and are willing to continue their support to priority requirements.

A number of conclusions were drawn up for action by GEMSI relating to the need for firm agreements on the international efforts, the dissemination to the world marine community of information on the availability of relevant reference materials, the publicizing of the work in the International Standards Organization (ISO-REMCO) and the difficulties being experienced by developing country marine laboratories in obtaining reference materials. A sessional sub-group was convened to examine these matters as well as those related to problems of terminology, GEMSI's continuing role and the future work programme in this field. Annex VII is a report on the meeting of this group.

3.6 OPEN-OCEAN BASELINE

Dr J. Michael Bewers introduced paper IOC/GGE(MSI)-VI/16 entitled "The design of an open-ocean baseline survey for trace metals in the Atlantic Ocean" by P.A. Yeats, J.O. Blanton and J.M. Bewers. The document reassesses the previous GEMSI proposals on this topic made at GEMSI VI in the light of scientific developments, and specifically, the improvement of the quantity and quality of trace metal determinations in seawater, during the intervening years. The revision re-advocates examination of the trace metal composition of North Atlantic Ocean, deep-water masses and their sources. It provides a rationale for this activity showing where it would be useful both for mass-balance assessments and for better understanding of source-related effects on the composition of deep waters. The document further advocates the assessment of major surface current composition and metal distributions in surface waters through the occupation of transects from coastline to deep ocean stations in order to gain an appreciation of the envelope of variability in metal, metal/ nutrient and metal/salinity relationships.

After some discussion regarding the practicality of conducting this type of large survey, the requirements laid down by GIPME V, and some aspects of the strategy in the context of mass-balance construction, it was decided to establish a sessional sub-group to consider future action $\underline{vis}-\underline{\dot{a}-vis}$ the deep ocean baseline proposal. The results of discussions of this sub-group (see Annex VIII) will be used as the basis for Dr Bewers to finalize the document.

3.7 REVIEW OF REFERENCE METHODS

Dr Duinker reported on discussions between Dr. Stephan Keckes, Dr Kullenberg and himself at Geneva (June 1985) related to the review and development of UNEP/Regional Seas Reference Methods. The agreement reached at GEMSI-VI regarding procedure involved in the review of Reference Methods (as described in IOC/GCE(MSI)-VI/3, Annex VI) was considered appropriate. The coordinators for the review of manuals sent to the IOC or UNEP Secretariats are Drs. Burns, Duinker and Bewers.

It was noted that repetition in analytical methodology in various Reference Methods could le avoided by the development of specific sections on, for example, the determination of organochlorines in any sample extract, describing chromatographic separation and electron capture detection which would be identical when analyzing various matrices. Similar procedures might be developed for trace elements (eg. describing AAS or ASV determinations).

4. <u>REVIEW OF METHODS, STANDARDS, INTERCALIBRATION AND TRAINING IN</u> REGIONAL COMPONENTS OF MARPOLMON AND REGIONAL SEAS ACTION PLANS

The IOC Technical Secretary described the activities which had taken place during the past intersessional period of GEMSI, referring to the description contained in the report of the Third Session of the Officers of the GIPME Programme, 15-17 July 1985.

He expressed the opinion that the past intersessional period of GEMSI had been productive and almost all of the activities projected at the Sixth Session had been addressed; despite the limited resources, the GEMSI Programme had progressed. A significant factor in this progress had been the close cooperation between IOC and UNEP. The limited resources, both financial and manpower, had affected operational activities (workshops, intercalibrations and training courses) and indeed many of these have been postponed until 1986 (see Agenda Item 5.2). As such, the

calendar of events for the next intersessional period will place enormous strains on the IOC Secretariat and, depending on the extent of GEMSI involvement, on individual experts assisting with these programmes.

In addition to the rescheduled operational elements of the GIPME Programme, as well as a number of activities of the UNEP Action Plans, there have been several extensions to other regions and activities. The WACAF/2 Programme is gaining momentum and a very recent workshop in Dakar, Senegal, has identified priorities. Additional activities have come under the responsibility of the IOC Secretariat in the Mediterranean and CPPS regions. GEEP is making progress and plans are well underway for conduct of a major biological effects workshop. (See Agenda Item 10).

As a guide to the Group, an envisaged timetable of activities for the coming intersessional period is contained as Annex IX.

5. REVIEW OF INTERCALIBRATION EXERCISES

5.1 INTERSESSIONAL IOC/UNEP EXERCISES

Dr Anthony Knap presented an overview on the IOC/UNEP supported intercalibration exercise for DDPH in seawater and tar on beaches, held in Bermuda, 1-15 December 1984. There were 15 participants. The programme had an associated training component, as well as in-depth investigation of large volume samplers and GC and GC/MS analysis of the extracts. The evaluation of Manuals and Guides Nº 15 on the sampling and analysis of the sea surface microlayer was also carried out. The results indicated that the methods outlined in the Manuals and Guides Nº 13 are a good guide for the detection of hydrocarbons in the marine environment. The measurement of beach tar is diagnostic for the presence of petroleum residues. The UV-Fluoresence method outlined is extremely sensitive for the analysis of hot spots and reproducible measurements can be achieved with a modest amount of chemical expertise. The interpretation of results from UV-Fluorescence is difficult and there is a need for representative reference materials with which to compare signals from extracts of environmental samples in general, and seawater extracts in particular.

In the absence of Dr. Joan Albaiges, whose arrival was delayed due to an airline strike, Dr. Knap presented a report on the IOC CSIC-UNEP Intercalibration Exercises for Oil and Petroleum Hydrocarbons, Barcelona, 11-17 November 1984, MEDCAL I. The Workshop consisted of lectures and presentations on sea surface microlayer sampling, tar on beaches, UV-Fluorescence analyses of seawater, and on sediments. Data was presented on eight samples of seawater analysed during the Workshop which showed a similar standard deviation as those achieved in the Baltic Intercalibration Exercise. Analysis of a sediment reference material was also carried out by gas chromatography and UV-Fluoresence.

The following recommendations were summarized from the report of MEDCAL I:

Beach tar measurements may yield valuable information on tar and should be related to floating tar. Microlayer studies are useful in understanding biogeochemical significance and MEDPOL should provide support for such studies. A musselwatch programme for the area. Reference materials for petroleum hydrocarbons be made available. GEL should review the suggested changes to Manuals and Guides Nos 11 and 13. IOC/UNEP should establish training programmes within the area and that intercalibration exercises be carried out at least once a year.

5.2 PROJECTED EXERCISES

The IOC Technical Secretary informed the Group that a number of intercalibration exercises were projected for 1986.

In support of the CARIPOL Monitoring Programme for petroleum hydrocarbons and as a follow-up to a planned training workshop on petroleum hydrocarbons in marine biota and sediments (Puerto Morelos/Cancun, October 1986) an intercalibration exercise has been planned. Concern has been expressed that scientists in the region should coordinate such exercises (and thus gain experience), and it is proposed that a suitable uncompromised material and an appropriate certified reference standard be distributed by Dr Jorge Corredor (University of Puerto Rico) in consultation with GEMSI in general, and with Dr. Knap in particular. The participants of the consultations in Solomons (Chesapeake Biological Station, University of Maryland, 1-3 November 1985) who made these recommendations, were informed of the status of the GEMSI ad hoc Group on Standards and Reference Materials and hence have a current awareness of which materials exist and may be suitable. Sufficient funds are available within the UNEP Project and JOC commitment to support CARIPOL for this follow-up exercise. GEMSI is requested to supply advice on the types of reference materials suitable for this exercise.

The second round trace metal intercalibration for marine organisms in WESTPAC (COBSEA, SPREP) was discussed at the previous GEMSI Session. The material for this exercise has not been prepared by ILMR owing to the long incapacitation of Dr Aston. The network for distribution of this or another material has been established with Dr Kwang Lee (Republic of South Korea) and Dr. John Brodie (University of Fiji) acting as coordinators for WESTPAC and SPREP, respectively. Dr Topping has been providing advice on the conduct of the exercise in view of his experience in organizing the first round intercalibration and it is expected that the final analysis of the results would be undertaken by GEMSI at a future session. Since there is slippage in the calendar of events' in WESTPAC, it was felt that an explanation should be communicated to the Task Team via this meeting, together with a suggestion of how to proceed effectively. This may involve finding another source for this material (eg. the materials known to be available in Japan or elsewhere). Perhaps an approach could be for GEMSI or the IOC Secretariat to formulate the appropriate letters requesting materials and informing the coordinators and the Task Team.

An intercalibration workshop is planned for petroleum hydrocarbons in the Mediterranean, to be convened in Barcelona, in September 1986, and will be carried out in cooperation with ILMR using UNEP/MAP funds. Also, an intercalibration exercise for petroleum hydrocarbons in marine sediments is being carried out in cooperation with IAEA/ILMR.

In the South East Pacific Region (CPPS) an intercalibration exercise has been initiated by 15 cooperating laboratories in the region. IOC has been requested to provide the technical backstopping to this exercise with the engagement of experts from the region. No details are presently available on the materials currently being distributed by Dr Alfonso Vasquez-Botello (Mexico). This exercise precedes a planned training workshop on petroleum hydrocarbon monitoring in the region for which Drs. Albaiges and Botello have been appointed instructors.

Finally, in the report of the recent WACAF Workshop (Dakar), reference is made to the conduct of intercalibration exercises in the region but no specifics are requested of GEMSI at present.

Dr. Fukai raised the question of who will provide hydrocarbon materials on a routine basis in the future. The ILMR has performed limited work in this field but is not able, at the present time, to provide materials on a wide basis. The Laboratory has been involved in petroleum hydrocarbon analysis with a commitment to the KAP region and has, in the past responded to UNEP requests concerning the Mediterranean Action Plan where IOC was considered to be the lead agency on petroleum monitoring. It was pointed out that the Barcelona Laboratory, under the direction of Dr. Albaiges, was being increasingly called upon to meet the needs for training and intercalibration in the Mediterranean Region.

Dr. Fukai clarified the position regarding the preparations for the second round trace metal intercomparison exercise in WESTPAC and reported that mussel and shrimp homogenates are available and that these would meet the requirements for the trace metal intercalibration. A small sub-group was appointed to review the preparations for distribution of the materials, including attachments in the form of work sheets describing the preferred methodology, the sample matrix and copies of the reporting formats. In addition, standard solutions of trace metals should accompany the intercalibration materials. It was estimated that approximately 100 kits would be required for this joint regional exercise.

It was recommended that attention be paid to the identification of petroleum hydrocarbon intercalibration materials which would meet the growing requirements in the various regions and their activities and that some common approach to the provision of these be established. These should also include the selection of appropriate certified reference standards (pure compounds) of, for example, PAH's or selected alkanes.

5.3 EXERCISES OF ICES AND OTHER ORGANIZATIONS

The ICES representative, Dr Bewers, provided a summary of intercalibration exercises being conducted, or planned within the ICES Community. An intercomparison for metals in estuarine water (6/TM/SW) for the Oslo and Paris Commissions will be conducted in 1986. Samples will be collected from the Rhine and Scheldt Estuary for homogenization and subsequent distribution to the Joint Monitoring Group and ICES laboratories. The collection of this material may provide an opportunity also for the preparation of an estuarine water reference material for trace metals. The collection programme will be followed by the occupation of a longitudinal estuarine transect in order to provide information on the distribution of metals in the entire river/estuary/coastal zone area of the chosen sampling region, so as to be able to place the actual levels of metals in the intercomparison samples in the context of conditions at OSPAR JMP (Oslo and Paris Commissions Joint Monitoring Programme) sampling sites.

The final report of the ICES first-round intercalibration for trace metals in sediments (1/TM/MS) being run by Bedford Institute of Oceanography (Dr. Douglas Loring) will be presented to the ICES Marine Sediment Working Group (Chairman: Dr Windom) prior to final publication. The results of this experiment should enable a far better understanding of the comparability and differences between various sediment digestion techniques.

The Oslo and Paris Commissions continue to request ICES to provide advice on the measurements of PCB's in marine sediments. In view of the need to resolve some outstanding problems with the choice of PCB analysis techniques and approaches, particularly in regard to standardization procedures, ICES has not yet been able to provide substantive new advice on this subject. This situation is entirely analogous to the situation vis-à-vis UNEP's OCA Programme requirements and GEMSI's advice.

The ICES Marine Chemistry and the Marine Sediment Working Groups have jointly completed an intercomparison for the measurement of trace metals in suspended particulate matter (SPM). Participation was restricted to a few laboratories having direct experience in SPM analysis and the results show surprisingly good agreement for a range of trace metals. This opens up the possibility of paying greater coordinated attention to SPM in future monitoring activities and ICES expects methodology for both quantification and analyses of SPM to assume greater importance in its future marine chemical activities.

Intercalibrations asociated with the ICES Baseline Study were described at GEMSI VI and did not need further explanation here. The Oslo and Paris Commissions had repeated their request for the early design and execution of an intercalibration for petroleum hydrocarbons in seawater. The ICES Marine Chemistry Working Group had been requested to undertake this task at its next meeting in Helsinki, February 1985.

Finally, the increased interest in standardizing the analyses of marine mammal tissues for organochlorine compounds was noted. This interest stems from a recognition of the incidence of diseases in marine mammals that might be related to organochlorine compounds in the tissues of these animals. The Marine Chemistry Working Group is being asked, at the request of the Marine Mammals Committee of ICES, to conduct an intercalibration for the measurements of organochlorines in seal blubber.

6. REVIEW OF RELEVANT REGIONAL WORKSHOPS AND TRAINING COURSES

6.1 INTERSESSIONAL WORKSHOP RESULTS

An account of the IOC-UNEP Workshop on Petroleum Hydrocarbons, Bermuda, 1-15 December 1984 was provided by Dr Knap under Agenda Item 5.1.

The Group considered the publication of original elements of such workshops in the open literature and it was reported that a publication covering the Bermuda Exercise was being submitted to the Marine Pollution Bulletin.

As a general comment on the conduct of workshops, it was remarked that the Barcelona Workshop was too condensed and that the time constraints of that exercise had not allowed for a fully-fledged intercalibration.

An important aspect of such workshops should be to critically evaluate methodology or reference methods and that a feed-back mechanism should exist whereby methods can be continually updated on the basis of findings of field trials.

On this basis, it was felt that the recommendations of both the Bermuda and Barcelona Workshops did not necessarily point to the immediate amendment of Manuals and Guides N^o 13 and that the sub-group on individual contaminants would be addressing any major update (eg. methods involving synchronous scanning).

The recommendations arising from the Barcelona Workshop concerning the analysis of petroleum hydrocarbons in sediments, were largely felt to be valid and that these would be considered in a major effort of the Group to provide a reference method in the UNEP Series based on the IOC Manuals and Guides Nº 11.

A brief account was provided of the Training Course on Chlorinated Hydrocarbon Analyses for Regional Seas participants, held at ILMR June 1985. The training course, with Dr. Robert Riseborough as Coordinator, was organized in response to a request from Mediterranean countries and was considered to have been highly successful in training participants in capillary GC techniques. It was pointed out that this was purely a training exercise of four or five weeks' duration with the ILMR staff devoting their full time.

Dr Fukai indicated the laboratory's preference to conduct one or two training courses each year (with 5-10 participants) rather than responding to <u>ad hoc</u> training requests of scientists.

While these training courses could be provided to all of the regional programme areas, they will mostly be centered on the Mediterranean, KAP, WACAF and East African regions. The next training course on trace metals will be held in March-April 1986.

Dr Knap reminded the Group that the Annual Bermuda Biological Station Training Course on the Analysis of Marine Pollution had trained 12 scientists the previous summer. Many of the participants were from the Caribbean Region and IOC and UNEP had provided valuable support. Up to 80 requests a year were being received; it is envisaged that 16 may be supported next year.

6.2 PLANNED IOC AND UNEP TRAINING ACTIVITIES

The IOC Technical Secretary provided an account of the preparations for the IOC/UNEP Organochlorines Workshop to be held in Port Moresby, Papua New Guinea with the participation of scientists from WESTPAC, COBSEA and SPREP

He pointed out that emphasis was currently being placed on the analysis of organochlorine insecticides (and less on PCB's) in mussel tissue in line with plans to develop a regional Musselwatch.

A meeting with the on-site coordinator, Dr. D. Mowbray, in Manila April 1985, had produced agreements on participants and course content.

IOC had provided teaching materials and reports pertinent to the Workshop, including an updated version of Reference Method Nº 14 to enable Dr. Mowbray to assemble a package of teaching materials in advance of the Workshop. He still requires a copy of a chapter on organochlorine analysis that has been prepared by Dr. Duinker.

IOC has agreed to provide two consultants to assist in the Workshop and to cover all aspects of sampling/sample preparation and clean-up and analysis by packed column gas chromatographs.

The Chairman of GEMSI has been requested by UNEP to organize the production of a manual on capillary techniques and to provide instruction in these techniques at the Workshop.

The IOC Technical Secretary stressed the need for adequate reference materials for this Workshop and indicated that particular attention should be paid to the procurement of a suitable suite of organochlorine insecticides. The availability of such materials is summarized in the report of the <u>ad hoc</u> Group on Reference Materials. Dr. Walton reminded the Group of the offer of NBS to support the Workshop. The availability of instrument performance standards was also mentioned in this context. An important training exercise should be the production of secondary reference materials from primary materials or certified reference materials.

A brief account was provided of the planned IOC-UNEP Workshop on Petroleum Hydrocarbons, Puerto Morelos, Mexico, October 1986. Details of the planning of this Workshop were provided in the report of CARIPOL Consultations, 1-3 November 1985. The Workshop would cover the analysis of petroleum hydrocarbons (PAH's in particular) in mangrove oyster and sediments with an introduction to organochlorine insecticide analysis. Activities and draft project proposals for follow-up and establishment of a network of laboratories for a regional Musselwatch were being discussed by scientists in the Caribbean Region.

The observer from NOAA, Dr John Calder, indicated that his organization (ie. NOAA) was making plans to extend their trend monitoring programme to Puerto Rico and the Virgin Islands and suggested that the CARIPOL Steering Committee establish contact with this Programme.

A number of concerns were raised regarding the course content and whether the appropriate materials existed or could be prepared in time, particularly the manual on individual PAH's in sediments (and Liota). It was noted that Dr Donald Atwood, Chairman of CARIPOL, would be overall coordinator, with Dr. Albaiges the principal course instructor. GEMSI was being requested to assist in the provision of the appropriate teaching materials and reference chemicals and standards. Again, it was noted that a degree of harmonisation of these aids was required.

The same principles applied to the proposed Workshop on Petroleum Hydrocarbons planned for the CPPS Region for which IOC is responsible as well as for the exercise planned in Barcelona, September 1986. It was also noted that the regional programmes, investigating petroleum hydrocarbons were proceeding with their analytical programmes, perhaps in advance

of the recommendations of GEMSI, and the speed with which methods had been confirmed or satisfactorily calibrated elsewhere (cf. IOC-UNEP-ICES-NOAA PAH Exercise). It was further pointed out that additional Spanish speaking expertise working with GEMSI would be a future requirement in the programme.

The questions regarding the suitability of present manuals and materials were referred to the appropriate <u>ad hoc</u> Sessional Group.

Information was provided on funds possibly available from UNEP for the provision of equipment, if these could be ordered before the end of the year for use in the forthcoming regional activities. The needs and requirements for all the above workshops were reviewed by the same sessional Sub-Group and a set of recommendations is contained in Annex X. Concern was expressed that 1986 had a very full agenda of activities for the IOC and that serious attention should be paid by GEMSI to establishing a common streamlined approach which would be of benefit to all regional coordination.

7. REQUIREMENTS FOR FUTURE REFERENCE METHODS

It was recognized that Reference Methods (see Annex XI) will be required for a considerable number of chemicals in various matrices. This requires the formulation of priorities. These have not yet been formulated in details, but this is to be expected in the near future, involving those related to estuarine environments as well.

Dr Fukai informed the Group that a meeting of the Expert Group on Land Based Sources will take place in December 1985. This will allow the definition of new Reference Methods to be developed in 1986. Dr Fukai will inform the IOC Secretariat on these priorities and also identify the Reference Methods to be developed under the guidance of the GEMSI Chairman as described under Item 3.7. Dr Fukai will discuss and report on the form of future Reference Methods with respect to the points raised under Item 3.7.

It was considered desirable that before the development of Reference Methods is undertaken, it should be defined clearly what type of application the methods would be used for.

8. METHODOLOGICAL ASPECTS OF MASS BALANCE AND FLUX STUDIES

8.1 RIVERINE AND ATMOSPHERIC FLUXES OF CONTAMINANTS

The discussion was directed into separate discussions of riverine and atmospheric inputs.

8.1.1 <u>Riverine Inputs</u>

The Group took note of the report of the GESAMP meeting in Roscoff on Land Sea BoundaryFluxes of Pollutants (WG 22). Dr Windom reviewed the formation, progress and aspirations of the group. The importance of Dr. Webb's contribution as a hydrologist was emphasized in terms of providing an exchange of interdisciplinary ideas. The extreme difficulties associated with the quantification of short-term processes such as storm transport of particulate matter was discussed but not resolved. The significance of regional effects was also noted with Dr. Knap emphasizing, for instance, the regional variability of application of synthetic organic pesticides.

Dr Windom noted that the strategy of only considering a few very large rivers was flawed, especially on a regional scale, but also on a global scale, because large rivers may carry a disproportionately small contaminant load since they are generally located in sparsely populated areas. In addition, the relatively long water residence times in large rivers and estuaries, compared to small systems, may fundamentally alter the estuarine processes.

Drs. Duinker and Bewers emphasized the potential use of distribution coefficients in modelling estuarine processes and suggested more studies be done on this subject. Dr Windom noted that, after having defined the inshore boundaries of rivers, the GESAMP WG 22 had now decided that its primary task would be to provide specific advice on methods to determine gross inputs to estuarine areas on regional and global bases. Some generic advice on methods to estimate net fluxes would also be produced.

The GEMSI group noted with satisfaction the work of the GESAMP WG 22 and wished it well in its deliberations.

8.1.2 <u>Atmospheric Inputs</u>

The discussion began with a consideration of atmospheric inputs of trace metals. Dr Timothy Jickells pointed out that the Sea Air Exchange (SEAREX) and Western Atlantic Tropospheric Exchange (WATOX) Programmes were now generating important data on the wet depositional fluxes of trace metals to the Pacific and N.W. Atlantic Oceans. It was felt that adequate methods for the collection, analysis and interpretation of trace metal concentrations of precipitation in rainwater from remote regions were now available. It appears that within a few years, adequate data for an assessment of the scale of atmospheric trace metals will be available for the NW Atlantic and much of the Pacific Oceans. Few data collections are planned in the South Atlantic or Indian Oceans. Results to date suggest that, while short-term variability can be large, if a sampling programme extends over a long enough period (eg. several months), reliable data can be attained. The results suggest high altitude transport of fine particulate matter enriched in trace metals is important.

It was noted that there is a large data base on atmospheric particulate concentrations, but that uncertainties in estimates of dry deposition velocities mean that it is very hard to convert this data to flux estimates. Dr Walton suggested that a review of older studies on the fallout of radionuclides may offer a solution to this problem.

The Group concluded that there is good evidence to suggest that atmospheric fluxes may now dominate the geochemical cycles of Pb and Hg. For other trace metals, it is likely that atmospheric inputs may be of major significance on a regional scale, but probably not on a global scale.

The discussion then moved on to organic contaminants with Dr. Knap providing an overview of the WATOX Programme and Dr Duinker of studies being conducted at Kiel University. The greater importance of dry over wet deposition for organic compounds was noted. However, it was explained that this distinction between vapour and particulate phase trace organics is difficult since significant evaporation from particulates on the filter can occur during sampling.

The matter of drawing up guidelines on how to proceed on assessing atmospheric fluxes was referred to the <u>ad hoc</u> Group on River inputs.

8.2 FLUX OF CONTAMINANTS TO THE SEA BED (SEDIMENT TRAPS)

Dr Andersen, reporting in the absence of Dr. John Farrington, outlined the major US programmes involved in flux studies of particulate materials. There are mainly four programmes, with only one dealing specifically with contamination assessment; the Shelf Edge Exchange Processes (SEEP) Programme of DOE. This effort is concerned with energyrelated products. The other programmes are the Vertical Exchange Experiment (VERTEX) in the NE Pacific, two Woods Hole efforts of Drs. W. Deuser and Dr S. Honjo concerning a wide geographic area, and an acelian dust air/sea interaction programme which is complementary to SEAREX. This hater programme is being conducted by Drs. Betzer and Duce of the University of South Florida and URI respectively. Dr Andersen pointed out that there were also numerous scientists conducting flux studies on an individual basis.

There are three main devices used in flux studies (i.e. cone, cylinder and free floating particle-intercepting traps). PARFLUX (the Panamana Basin Experiments), was a programme that showed that these devices are comparable. In situ pumping devices are also used, but the relationship between these and sediment traps have not been completely resolved. All of these devices are well reported in the literature. Dr Andersen also mentioned activities of other countries with respect to sediment/particle flux programmes.

Dr. Knap pointed out that many of these devices are designed for natural product biogeochemistry and not conamination assessment. However, this may be resolved by careful consideration of the materials used for manufacture. A general discussion enforced the usefulness of data collected by the analysis of trap-collected material and how atmospheric/oceanic residence times can be calculated leading to the calculation of mass balances. Also the fact that sample sharing of this collected material to a wider scientific audience would lead to a far more cost-effective assessment of contaminants in the marine environment.

An important specific need is the design of a pumping system for the analysis of partitioning (particles/dissolved) of trace organic compounds in the deep ocean. This will then lead to the inclusion of trace organics in the open-ocean baseline programme (Item 3.6).

8.3 GLOBAL AND REGIONAL FLUX STUDIES

Dr Andersen briefly outlined the present status and immediate plans of the US Global Ocean Flux Study (GOFS). The programme is essentially a biogeochemical research effort addressing the production, flux and fate of biogenically produced compounds. He pointed out that a steering committee had been formed under the chairmanship of Dr. Peter Brewer of the Woods Hole Oceanographic Institution. Several meetings had been convened and presently there are two sub-groups that are developing plans for undertaking pilot programmes; one for the North Atlantic Ocean and one for the North Pacific Ocean. These efforts are to provide the necessary preliminary foundation for having GORS become operational in the early 1990's. It is hoped that the schedule that will be followed, will mesh with placing the Ocean Colour Imager (OCI) in orbit, for synoptic coverage of measurements relating to productivity which is an essential element of GOFS. GOFS is very closely associated with the World Ocean Climate Experiment (WOCE) in being one of several global studies being developed in the US.

Other efforts addressing the flux of material through the ocean environment were also noted, particularly those being undertaken in the UK and France, where informal coordination was already being conducted betwee NERC, CNRS and NSF.

Dr Knap pointed out that, at least with regard to the US effort, the driving force for the programmes was not that of assessing contamination. He pointed out that if proposals were generated for this, they would never pass the pier review system. Dr Andersen further stressed this, pointing out that it is a major reason for giving attention to characterizing the collection of marine contamination data of interest to GIPME in the context of research efforts being conducted by the Member States of IOC and of UNEP. He pointed out that he stresses this point to all governing bodies of IOC when presenting the GIPME Programme.

8.4 REGIONAL MASS BALANCE CALCULATIONS

Dr Andersen noted that at the Third Session of the GIPME Group on Policy, Planning and Strategy (GOPPS), the officers of GIPME discussed the use of MARPOLMON data in gaining a further understanding of fundamental biogeochemical processes. He indicated that GOPPS felt that GEMSI should give due consideration for seeing if mass balance calculations could be made using an existing data base for some region. He noted that the Mediterranean was such a region, and suggested that it be used. A sessional sub-group under the chairmanship of Dr. Bewers was established to address this charge of GOPPS intersessionally. However, if data from the Mediterranean were to be obtained for use in mass balance calculations, certain considerations regarding this data should be borne in mind. These are contained in Annex XII.

9. QUALITY ASSURANCE (QA) OF REPORTED DATA

The Chairman asked members to report on intersessional activities concerned with quality assurance studies. Dr. Topping opened by giving an account of the proposals that had emerged from discussions of QA within the ICES Marine Chemistry Working Group (MCWG). The group had recognized the role of reference materials in maintaining the quality of analytical data and had suggested that additional certified reference materials and uncompromised reference materials (URM) should be prepared for this purpose. They specifically recommended that URMs be made available to participants in cooperative monitoring programmes of contaminants in fish and shellfish so that regular checks could be made on the analytical performance of laboratories over a period of time.

In the 1985 report of MCWG, the trace metal subgroup had prepared a list of required Chemical Reference Materials (CRM's) and URMs for both seawater and biological tissue. It was felt that this list might be useful for the GEMSI ad hoc Group on Reference Materials in their subsequent discussions in the ICES Marine Sediments Working Group (MSWG). He reported that the MSWG had independently reached the same conclusion as MCWG on the need for for additional RM's and the use of URM's in the role of in-house quality control. Dr Calder then gave an account of the approach US-NOAA was taking to QA work and the role that ICES participants had played in the establishment of their QA scheme. He reported that Dr Shire Berman (NRC) had been contracted to prepare suitable trace metal reference materials for NOAA laboratories and that he would inquire whether these could be made available to laboratories involved in the IOC/UNEP Regions. On behalf of ILMR, Dr Fukai gave an account of intercalibraiton studies organized by his laboratory and the role these had played in the evaluation of data from the cooperative monitoring studies of MEDPOL and other UNEP/OCA Programmes. He stated that laboratories which did not participate in these intercalibration programmes did not have their data included in the evaluation exercises. Unlike ICES countries, where there appeared to be a better set of comparable data, he stated that one of the problems of poor comparability in UNEP's OCA Programme was the lack of continuity of analytical staff, caused primarily by trained technicians leaving laboratories for other positions.

During subsequent discussions on this topic, it was generally agreed that QA studies should also be concerned with the general approach for collecting acceptable data, ie. sampling, storage and analytical procedures. In this context, Dr. Bewers reminded the Group of the proposals made by ICES for the establishment of trace metal sea water reference stations to provide a check on the comparability of sampling and storage procedures in trace metal surveys in sea water.

The group then addressed the question of what guidance could be given to laboratories in UNEP'S OCA Programme on good laboratory practice in relation to QA work. Dr Topping informed the group that the matter had been raised by Chemists at MCWG who in general felt that there was sufficient comprehensive documentation on this subject which could be referred to these laboratories. A list of relevant publications had indeed been prepared and annexed to the 1985 MCWG report. Dr Topping agreed, however, that such references may not be easily obtained by laboratories in developing countries and that those that could obtain them might not consider them appropriate at their present level of experience. He considered that perhaps a summary document should be prepared by GEMSI outlining the key elements of good QA practice in relation to the request for advice on this topic. The Chairman asked Dr. Yopping to coordinate a sessional sub-group to address the preparation of such a leaflet (see Annex XIII).

10. <u>COOPERATION WITH THE GROUP OF EXPERTS ON THE EFFECTS ON</u> POLLUTANTS (GEEP)

In the absence of the Chairman of GEEP, Dr Brian Bayne, the Chairman of GEMSI asked Dr. Andersen to report on the progress being made by GEEP. Dr Andersen reported that GEEP had had its first meeting in December 1984 and that it had prepared plans for convening a biological effects workshop in Oslo in 1986. Final arrangements for the workshop would be made at the second meeting of GEEP planned for December 1985. The participants in this workshop, numbering 20-26 scientists, were recognized experts in the field of biological effects measurements and their principal task will be to conduct laboratory and field comparisons of a number of methods which had been identified as suitable for this type of work. He also reported that the Government of Venezuela had invited GEEP to conduct a field trial of their measurements in one of its marine parks to study the vulnerability of this type of environment. He also informed the Group that GEEP was to contribute to the GEMSI questionnaire on musselwatch activities by providing a short questionnaire on biological effects measurements.

The ICES representative stated that ICES had been notified of plans for the GEEP workshop and was intending to collaborate with IOC/ GEEP in the workshop phase of initial GEEP activities which logically extended from ICES' own investigations of biological effects methods. Provisionally, ICES plans to augment the GEEP workshop by the inclusion of fish pathology and disease studies and had proposed that Dr E. Egidius be asked to coordinate the ICES cooperation with GEEP in consultation with the Chairman of GEEP and Professor I. Dundas, who had chaired the recent ICES Study Group on Biological Effects Techniques.

Dr Andersen passed on a request from GEEP for GEMSI's assistance in the selection and use of appropriate chemical methods for assessing body burdens of contaminants in the organism being examined in the workshop. The Group recognized the need for close contact with GEEP in relation to this request, and it was suggested that this could best be served by a member of GEMSI attending the next meeting of GEEP, 2-6 December 1985, Paris. It was agreed that Dr Palmork should represent GEMSI at this meeting.

11. FUTURE INTERSESSIONAL ACTIVITIES

The Group agreed that the following <u>ad hoc</u> groups should continue their intersessional activities:

11.1 INDIVIDUAL ORGANIC CONTAMINANTS

Membership: K. Burns (Chairperson)

- J. Duinker
- M. Ehrhardt
- J. Farrington
- A. Knap
- K. Palmork

Intersessional activities of this sub-group are as follows:

- to revise Manuals and Guides Nº 11 with the aim of making it a UNEP Reference method;
- (ii) to prepare a list of suggested standard materials for individual organic contaminants;
- (iii) amendment of UNEP Reference Method nº 14 to include instructions on the use of capillary gas chromatography. A draft should be available for the Port Moresby Workshop;
- (iv) preparation of Standard Substances to be distributed for monitoring programmes for chlorinated hydrocarbons;
- (v) to prepare a position document for strategies to measure atmospheric deposition in the context of computing mass balances of organic contaminants;
- (vi) to continue analysis of environmental reaction products of organic contaminants with a view to producing a summary background paper during 1986.
- 11.2 MARINE ORGANISMS IN MARPOLMON (Musselwatch)

Membership: J. Bewers J. Calder G. Topping (Chairman) A. Walton H. Windom

See Annex V for the intersessional activities of this sub-group.

- 11.3 RIVER INPUTS
 - Membership: J. Bewers R. Dawson H. Dou J. Duinker M. Hungspreugs A. Knap J-M Martin

 - H. Windom (Chairman)

See Annex VI for the intersessional activities of this subgroup. 11.4 REFERENCE MATERIALS

Membership: J. Bewers

- J. Calder
- M. Ehrhardt
- R. Fukai
- G. Topping
- A. Walton (Chairman)

See Annex VII for the intersessional activities of this sub-group.

11.5 OPEN-OCEAN BASELINE

Membership: J. Bewers (Chairman) T. Jickells G. Topping H. Windom

See Annex VIII for the intersessional activities of this sub-group.

11.6 QUALITY ASSURANCE

| Membership: | J. | Bewers | |
|-------------|----|---------|------------|
| | J. | Calder | |
| | к. | Palmork | |
| | G. | Topping | (Chairman) |
| | н. | Windom | |

The intersessional activities of this group are to be as follows:

(i) to prepare a leaflet on good laboratory practice.

12. <u>ELECTION OF OFFICERS</u>

Pursuant torules of procedure of governing Expert Groups of IOC, the Group was required to elect its Officers for the next intersessional period and Bighth Session. For the purpose of electing the GEMSI Chairman, the meeting was referred to the IOC Technical Secretary. Dr Duinker was nominated and elected unanimously as Chairman for the next intersessional period and Bighth Session. The chair was then returned to Dr. Duinker. The re-elected Chairman invited nominations for the poisition of Vice-Chairman. Dr Palmork, the incumbent, announced his resignaiton. Dr Knap was nominated and elected unanimously. Dr Bewers then thanked Dr Palmork for the many years of dedicated service he had provided to GEMSI.

13. OTHER MATTERS

13.1 MARINE MAMMALS

The Chairman of GIPME, Dr. Andersen, introduced this topic by referring to the request for ICES and IOC to contribute to the FAO/UNEP Global Action Plan for the Conservation, Management and Utilization of Marine Mammals. This matter had been discussed by GOPPS, and GEMSI and GEEP had been requested to consider what issues, in respect of marine mammals, might be addressed by these two Groups. It was agreed that matters related to the occurrence of contaminants in marine mammals as sentinel organisms were the responsibility of GEMSI, whereas the assessment of effects on marine mammals fell within the sphere of interest of GEEP. It was accepted that while marine mammals were able to accumulate contaminants, particularly those having affinity for fatty tissue, to high levels, it was unlikely that mammals, <u>per se</u>, would be very suitable monitoring organisms because of their wide-ranging nature and the desire to protect them rather than sacrifice them for scientific or other purposes. Nevertheless, the use of marine mammals, acquired on an opportunistic basis (ie. occasional deaths, strandings, inadvertent entanglement in fishing gear, etc) were useful for the detection of contaminants having lipid affinity and low degradation rates, especially where such contaminants were of an ephemeral nature in other marine materials (eg. water, sediments, etc.).

The ICES representative then referred to recent discussions within ICES concerning the possible association between marine mammalian disease and the incidence of organic contaminants in their tissues that was of concern in the Baltic and some other areas of the North Atlantic. There had been a request to the ICES Marine Chemistry Working Group (MCWG) from the ICES Marine Mammals Committee for the conduct of an intercomparison of procedures for the determination of PCB's in mammal tissue, specifically blubber. This matter is to be considered by MCWG at its next meeting.

Drs. Knap and Duinker then referred to the results of recently completed work on organochlorine compounds in a variety of marine mammal tissues from several areas. This work was continuing on an opportunistic basis as Dr. Knap was proposing to conduct further studies of the tissues of two whales recently beached in Bermuda. Dr. Bewers had expressed particular concern regarding the methods of tissue contaminant extraction and sample clean-up in analytical procedures and Dr. Knap expressed a willingness to conduct tissue analyses by a number of methods using material obtained from the recently beached Bermuda whales. This would be extremely valuable to investigations in this topic and Dr. Knap's offer was gratefully accepted. It was agreed that the investigations of the analytical procedures should be conducted on a collaborative basis between ICES and IOC, and the results would be reviewed by MCWG at its next meeting. Dr. Bewers undertook to seek information on the details of currently-used analytical procedures for the analysis of marine mammal tissue and arrange to ensure that this information be provided to Drs. Knap, Duinker and Topping (Chairman, MCWG). Any intercalibration activities resulting from these discussions should involve both ICES and IOC laboratories.

13.2 SOUTHERN OCEAN BASELINE STUDIES

This item arises as a result of the interests of IOC Programme Group on Southern Oceans and of the Scientific Committee on Atmosphere Research (SCAR) in baseline measurements of contaminants in the southern oceans. It was noted that the proposal for a deep ocean baseline study includes the occupation of stations and transects in the South Atlantic, north of the Antarctic convergence. It was generally agreed that there exists a greater paucity of data for contaminants in the southern oceans than elsewhere but that there existed a capability to make at least measurements of trace metals, and possibly also hydrocarbons in this region if suitable ship time was available. It was agreed that, to the extent possible, the trace metal baseline study in the South Atlantic should be extended to regions south of the Antartic convergence. In seeking means to carry out the South Atlantic component of the baseline study, consideration would be given to the acquisition of measurements from more southerly stations.

13.3 COMMON MEETINGS BETWEEN IOC AND LCRS EXPERT GROUPS

There has been a suggestion, within the governing bodies of the IOC that GEMSI and the ICES Marine Chemistry Working Group (MCWG) meet consecutively at the same location instead of separately, as at present. This proposal was presumably based on an assumption that because these respective groups have several common members and have substantially benefitted from each other's quality assurance activities, there exists, and continues to exist, a predorinance of common goals and interests among the two groups. On closer examination, however, this justification is not as strong as might have been assumed, based on previous situations. Although GEMSI and MCWG did have six or seven common members in the late 1970's, by 1985 this number had declined to about four. It seems likely that this will further decline to two to three common members in 1986/1987.

The benefits that have accrued to each of the two groups as a consequence of activities in the other, were certainly such that closer formal (as opposed to <u>de facto</u>) collaboration would have been beneficial in the initial activities of the groups (ie. in the years 1976-1982). This was because both groups were trying to solve similar problems (of predominantly a sampling and analytical character) as pre-requisites to the design, establishment and execution of baseline and monitoring programmes. More recently (1983-1985), the two groups have found themselves dealing to a much greater extent with problems within their own spheres of interest. It is the interest of ICES in the North Atlantic area and the needs of the Oslo/Paris and Helsinki Commissions in conducting monitoring and assessments in their jurisdictional areas that has dominated the work of MCWG. In GEMSI, it is the requirement for assistance to regional IOC (and since 1984, IOC and UNEP) programmes that have received most attention. Since the relative states of development of the ICES area is rather different from that in the IOC and UNEP regional sea study areas, this has required rather different approaches and levels of sophistication in the respective activities of GEMSI and MCWG. Nevertheless, in cases of common goals being dealt with at similar levels of sophistication, GEMSI and MCWC have been able to complement each other very effectively without introducing any unnecessary duplication of effort.

Some additional factors also weigh against consecutive meetings of the two groups. First, MCWG often meets consecutively with other groups such as the ICES Marine Sediment Working Group or the Working Group on Pollution Baselines and Monitoring in the Northern Atlantic. Another consecutive meeting would require that the common members be absent from their home laboratories for a period of three weeks. This is an unreasonably long period. Second, any attempt to overlap the MCWG and GEMSItto reduce this period would also be fraught with difficulty because of the very large membership of MCWG (commonly 35-40 individuals). The combined group might number over 50. This is far too large a number for the effective conduct of any business.

GEMSI concludes, therefore that it would be undesirable to alter the present meeting arrangements for MCWG and GEMSI. The conventional separation of the two meetings permits more effective and considered use of each group's activities by the other group and these benefits should be maintained by adhering to the <u>status quo</u>.

13.4 OBSERVER ATTENDANCE

Dr Andersen pointed out that there has been increasing development in activities (eg. in contamination assessment) in the regional programmes of IOC and UNEP. It is anticipated that the trend will continue and increase and, in fact, is a pre-requisite for implementing MARPOLMON and achieving the objectives of GIPME. Based on these observations, he suggested that GEMSI and the IOC/UNEP Secretariats giving continuing attention to ensure that appropriate regional respresentation is present in future GEMSI meetings. He further suggested that the agenda of a particular meeting serve as the basis of identifying such participation. For example, he noted that the present meeting would have benefitted from Dr. Atwood's presence in his capacity as Chairman of CARIPOL.

14. ADOPTION OF THE SUMMARY REPORT

The draft Summary Report and Recommendations were adopted by the Group. The group gave editorial license to the Secretariat and Chairman to develop the final version based on the corrections received from the members at the Session.

15. <u>CLOSURE</u>

The Chairman, in closing the meeting, thanked the members for their usual enthusiastic participation over a long uninterrupted Session. He apologized that the Session with its full Agenda had required members to sacrificed the whole weekend. Special thanks were given to Dr Fukai, the Secretaries, Ms. Orano and Dr. Dawson. There being no other business, the Chairman closed the meeting at 12.00 hours on 19 November 1985.

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Annex 1

ANNEX I

AGENDA

1. <u>OPENING</u>

2. ADMINISTRATIVE MATTERS

- 2.1 ADOPTION OF THE AGENDA
- 2.2 DESIGNATION OF RAPPORTEURS.
- 2.3 CONDUCT OF THE SESSION

3. <u>INTERSESSIONAL ACTIVITIES</u>

- 3.1 THE ANALYSIS OF INDIVIDUAL ORGANIC CONTAMINANTS
- 3.2 THE USE OF MARINE SEDIMENTS IN MARPOLMON
- 3.3 THE USE OF MARINE ORGANISMS IN MARPOLMON (MUSSELWATCH)
- 3.4 RIVER INPUTS OF POLLUTANTS TO THE COASTAL ENVIRONMENT
- 3.5 THE AVAILABILITY OF STANDARDS AND REFERENCE MATERIALS
- 3.6 OPEN-OCEAN BASELINE
- 3.7 REVIEW OF REFERENCE METHODS
- 4. <u>REVIEW OF METHODS, STANDARDS, INTERCALIBRATION AND TRAINING IN</u> REGIONAL COMPONENTS OF MARPOLMON AND REGIONAL SEAS ACTION PLANS

5. REVIEW OF INTERCALIBRATION EXERCISES

- 5.1 INTERSESSIONAL IOC/UNEP EXERCISES
- 5.2 PROJECTED EXERCISES
- 5.3 EXERCISES OF ICES AND OTHER ORGANIZATIONS

6. REVIEW OF RELEVANT REGIONAL WORKSHOPS AND TRAINING COURSES

- 6.1 INTERSESSIONAL WORKSHOP RESULTS
- 6.2 PLANNED IOC AND UNEP TRAINING ACTIVITIES

7. REQUIREMENTS FOR FUTURE REFERENCE METHODS AND MATERIALS

- 8. METHODOLOGICAL ASPECTS OF MASS BALANCE AND FLUX STUDIES
 - 8.1 RIVERINE AND ATMOSPHERIC FLUXES OF CONTAMINANTS
 - 8.2 FLUX OF CONTAMINANTS TO THE SEA BED (SEDIMENT TRAP)
 - 8.3 GLOBAL AND REGIONAL FLUX STUDIES
 - 8.4 REGIONAL MASS BALANCE CALCULATIONS
- 9. QUALITY ASSURANCE OF REPORTED DATA
- 10. <u>COOPERATION WITH THE GROUP OF EXPERTS ON EFFECTS OF POLLUTANTS (GEEP)</u>
- 11. FUTURE INTERSESSIONAL ACTIVITIES
- 12. <u>ELECTION OF OFFICERS</u>
- 13. OTHER MATTERS
- 14. ADOPTION OF SUMMARY REPORT
- 15. <u>CLOSURE</u>

ANNEX II

RECOMMENDATIONS

RECOMMENDATION GEMSI VII-1

As the initial phase of, or as a pre-requisite to the conduct of an open-ocean baseline for selected organic contaminants in seawater, it is recommended that the effectiveness of techniques (eg. liquid-liquid extraction, liquid-solid absorption) that are used to pre-concentrate the analytes from large volumes of seawater be thoroughly tested and intercompared.

RECOMMENDATION GEMSI VII-2

The Eighth Session of GEMSI be organized after the Working Committee for GIPME in order to respond in a timely fashion to the requests of the parent body. The venue for the Session should be decided through consultations between the Chairman and the joint Secretariats, but noting that the Bermuda Biological Station and the Instituto Bio-organico, Barcelona have both kindly offered to provide facilities.

RECOMMENDATION GEMSI VII-3

That the IOC Secretariat finalise arrangements for the Workshop on River Inputs in Thailand in early 1986 according to the guidelines laid down in the report of the sessional subgroup on River Inputs (Annex VI). It is further recommended that the IOC Secretariat approach UNEP/GEMS with a view to seeking additional funding of this exercise.

RECOMMENDATION GEMSI VII-4

It is recommended that early attention be paid to the provision of adequate instrumentation to the key laboratories involved, should funds become available. The Group has provided a series of proposals (Annex VII) for consideration of the joint secretariats in support of the planned activities and envisaged needs.

RECOMMENDATION GEMSI VII-5

That in all future meetings of GEMSI, appropriate representation of regional programmes of the IOC and UNEP be ensured, as necessitated by the Agenda.

RECOMMENDATION GEMSI VII.6

That two members of GEMSI should attend the proposed IOC/UNEP training/intercalibration exercise in Port Moresby, Papua New Guinea in order to provide instruction in capillary gas chromatography for the analysis of individual organics. It is also suggested that UNEP prepare a draft reference method on the analysis of individual PCB congeners for this Workshop. IOC/GGE(MSI)-VII/3 Annex II - page 2

RECOMMENDATION GEMSI VII-7

That an addendum concerning the use of synchronous scanning spectrofluorimetry should be issued for Manual and Guides Nº 13. Manual and Guides Nº 11 on the Analysis of Petroleum Hydrocarbons in Marine Sediments should also be revised in consideration of results of intersessional work carried out by the group on individual organic contaminants.

RECOMMENDATION GEMSI VII-8

That a meeting of the <u>ad hoc</u> Group on Reference Materials (composed of producers and users) be held during 1986 under the chairmanship of Dr. Walton The purpose of the meeting will be:

- to puruse the publication of the document listing all available materials for use as standards, intercalibration and intercomparison purposes;
- (ii) to compose and priorize a listing of needed materials;
- (iii) to secure the cooperation of the producer organizations in meeting the needs as identified - to the extent possible;
- (iv) to develop the procedures whereby the various international organizations can ensure the distribution of material to laboratories - particularly those in developing countries.

RECOMMENDATION GEMSI VII-9

That the IOC and UNEP Secretariats, together with the officers of GOPPS initiate actions for the production of Guidelines for the Design and conduct of a programme to Assess Contamination in Marine Sediments based on the perceived needs within regional activities. The level of the manual describing these guidelines should depend on specific requirements in the regional programme.

RECOMMENDATION GEMSI VII-10

That appropriate action be initiated by the Secretariat to acquire a regional data base to allow GEMSI to undertake an assessment of mass balance calculations, as directed by GOPPS, bearing in mind comments contained in Annex XII.

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ANNEX III

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ANNEX IV

SESSIONAL LEPORT OF SUBGROUP ON INDIVIDUAL ORGANIC CONTAMINANTS

The following agenda items were sessionally discussed by the Subgroup on Individual Organic Contaminants:

1. BARCELONA WORKSHOP

The Group discussed the comments arrising from the IOC/CSIC-UNEP Intercalibration exercise for Oil and Petroleum Hydrocarbons held in Barcelona, 11-17 November, 1984. These comments were suggestions for changes to Manuals and Guides 11 and 13 in Section 7.1 of this report. Generally, the comments taken to be possible revisions for M & G 11 accepted. However, none of the comments was felt to be urgent enough to necessitate IOC reprinting the manual. The points can be changed in the next revision. These are addressed point by point as given in the Barcelona Report.

- (i) Page 5, Section 4, line 1 suggested amendment accepted.
- (ii) Pages 5-6, Section 5 suggested amendment accepted.
- (iii) Pages 7-8, Section 6 suggested amendment accepted.
- (iv) Page 11, Section 7.3 (sample collection and storage). Rejected as the new sediment strategy Manuals will include this.
- (v) Page 13, Fig. 5 (reject) the EPA tag is an example.
- (vi) Page 13 Section 8.1 suggested amendment accepted.
- (vii) Page 13 Section 8.2, line 2 suggested amendment accepted.
 (viii) Page 14, paragraph 2, line 5 suggested amendment accepted.
 - (ix) Page 14, line 2 change the weight to 50g and leave the internal standard section.
 - (x) Page 14 Section 8.4 line 1 suggested amendment accepted.

The Group also noted that as wet sediment is extracted, water was present and difficulties with methanol and water mixing were not to be expected. In Section 7.2 concerning Manual and Guides Nº 13, the general comments were considered not to be of sufficient concern to change the Manual.

- (1) Page 1, Section 1.1 the subject of opening the bottle underwater was rejected as experiments conducted with divers show that the surface film is destroyed by the dropping of the bottle through it, and that the escaping air from the bottle prevents inclusion of this material.
- (ii) Page 2, first four lines suggested amendment rejected, based on the 1984 Bermuda Workshop results, the cleaning outlined in the Manual is adequate.
- (iii) Page 2, paragraph 4 suggested amendment rejected.
- (iv) Page 2, paragraph 5 suggested amendment accepted.
 - (v) Page 9, Section 2.8 suggested amendment rejected, as this is a simple method, ie. detection of hot spots. "Clean-up" will introduce more contamination than helping to resolve problems in the methodology.
2. MANUALS AND GUIDES/UNEP MANUALS

2.1 EVALUATION OF PANCAL 1984 WORKSHOP AND FURTHER RECOMMENDATIONS ON METHODS FOR PETROLEUM HYDROCARBONS

Evaluation of data from the Bermuda Workshop showed that the materals of analysis of DDPH in seawater described in Manual and Guides Nº 13 could be used to provide a sensitive and precise measure of fluorescence under the conditions stated, but that in open ocean waters the UV-F signal does not necessarily correspond to the presence of petroleum of combustion product hydrocarbons in sample extracts. It was further shown that more accurate estimates of oil content samples contaminated by petroleum could be obtained if reference standards closely matched the type of oil in the samples. More information on sample composition could be obtained by expanding the method to include emission and synchronous excitation/emission scanning. Several other comments on methods printed in Manual and Guides Nºs. 11 and 13 indicated that an update of the sediment manual to include revisions and expansion is necessary. Thus the sub-group has undertaken to revise Manual and Guides Nº 11 according to the discussion summarized below.

2.1.1 <u>Sulphur Removal</u>

The extraction procedure as written Manual and Guides Nº 11 relies on the saponification procedure to remove elemental sulphur. The procedure in not adequate for all sediment types. A number of methods has been described in the literature, among them several employing the use of activated copper. A question arose as to whether the copper might also remove organic sulphur compounds from extracts and Dr Bhrhardt tested this in his laboratory. Passing a solution of dibenzothiophene in hexane through a copper column resulted in the complete recovery of the dibenzothiophene. In addition, Dr Albaiges has tested the recovery of a variety of organic sulphur compounds from extracts which are useful indicators for source determination. It is not clear, however, how effective activated copper is in removing elemental sulphur and how long and under what conditions its activity can be retained. Even if no signal related to elemental sulfphur is detected by an FID, enough elemental sulphur may still be present to seriously interfere with the performance of an electron capture detector. If an ECD is to be used, it may be more advantageous to remove elemental sulphur by sharing the sample solution with a droplet of mercury. Work is continuing at the Kiel laboratory to resolve this question.

2.1.2 Extract Clean-Up

The Group agreed that the procedure for removing biogenic lipids from samples was inadequate as described in Manual and Guides Nº 11. Thus a more rigorous procedure will be added. This will be discussed intersessionally by Dr. Burns and Dr. Knap.

2.1.3 Sediment Type

Since the retention of organic contaminants in sediments depends on sediment type and organic carbon content, the Group recommended that a brief description on how to sieve and characterize basic

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sediment type should be included in Manual and Guides Nº 11. This will be provided by the Sediments Sub-Group as well as a procedure for the determination of organic carbon. Specific reference will be made to the strategy guidelines now in preparation. (Dr. Knap).

2.1.4 UV-F Procedure

The text will be expanded to cover scanning techniques, and appropriate figures illustrating data interpretation will be included. (Drs. Knap and Burns).

2.1.5 Quality Control

An example of the need for routine quality control and interlaboratory comparison will be included. (Dr. Palmork).

2.1.6 Standards

The Group stressed the need to distribute both analytical standards and reference materials to ensure the long-term quality control in individual laboratories. A list of recommended standards for PAN has been prepared and was presented at the IOC/UNEP meeting on Standard Reference Materials (Washington DC, 28-31 October, 1985). (Dr Ehrhardt).

The Group expressed its willingness to contract with UNEP to write a reference method for the analysis of petroleum hydrocarbon in sediments as requested by UNEP for use in its Regional Seas Programmes. The time scale is approximately one year.

The Group noted that Manuals and Guides Nº 15 (Procedure for sampling the sea-surface microlayer) was now in the literature and was used in part for the Bermuda, 1984 Workshop. This will be reviewed intersessionally by the Group at the next GEMSI meeting.

2.2 UNEP REFERENCE METHODS

2.2.1 <u>Reference Method Nº 14</u>

At the request of UNEP the Sub-Group re-evaluated the draft manual for the analysis of PCB's and DDT's in marine organisms. Dr Duinker reported on the interagency meeting in Geneva on Reference and Research Materials and informed the Group that UNEP has agreed to support the concept of individual component analysis for organic contaminants in Regional Seas Monitoring Programmes. Reference Method Nº 14, thus becomes an interim guide. Dr Fukai stressed that the capillary version was a high priority. A draft will be ready for the Papua New Guinea Workshop on the capillary column technique for CHC's. It was suggested that UNEP Reference Methods should take the analyst from samping of a specific matrix to clean up sample concentrates, and that other Reference Methods should describe the analysis proper (eg. capillary gas chromatography). The Group accepted this approach and, after discussion of specific details, prepared fruther revision to the document for transmission to UNEP. IOC/GGE(MSI)-VII/3 Annex IV - page 4

Discussion then followed on the selection of compounds the Group thought appropriate to recommend for monitoring purposes. Criteria for selecting individual contaminants were chosen as:

- (i) the ability of analytical techniques to resolve the contaminant from other interfering compounds, thus ensuring accurate quantification;
- (ii) significant occurrence of the component in source mixtures;
- (iii) known presence in environmental samples; and
 - (iv) priority placed on the most toxic components.

The Group noted that the ICES Marine Chemistry Working Group had selected a series on indiviual PCB congeners and recommended these as a first step in selecting candidate molecules. Dr Duinker pointed out that some of these compounds could not be resolved under known analytical conditions and thus they did not meet the first criterion for selection. He also pointed out that some of the PCB congeners known to be toxic fall into this category. Thus, priority should be given to further improvements in the analytical resolution. The Group discussed techniques such as optimizing the liquid phase composition and the use of two-dimensional gas chromatography. Dr Duinker agreed to compile a preliminary list of candidate molecules for PCB analysis after full evaluation of current data in the framework of the four selection criteria. The Group agreed to complete draft manuals based on capillary techniques in 1986.

The draft manual will spell out the problems and caveats and for the first case will show quanitification by individual component PCB's and technical mixtures.

2.2.2 Reference Methods Nos 16 and 17

In view of the development and implementation of high resolution techniques and the extreme necessity for state-of-the-art analytical procedures for seawater analysis, the Group recommends that revisions to Methods Nºs 16 and 17 allow for consideration of sampling/ extraction clean-up until the stage of sample injection. Reference Method 17 should be revised before Nº 16.

2.2.3 Reference Method Nº 24

This is a draft method for sampling of aerosols and wet precipitation for analysis of chemical pollutants, and will be considered by the Group intersessionally. It was noted that Method P: Determination of halogenated hydrocarbons in aerosols and in wet precipitation is being written by a GEMSI member and should be available in draft form for the next meeting of GEMSI. This will cover sampling analysis and clean-up.

3. <u>SUBGROUP ON LIST OF STANDARDS FOR INDIVIDUAL CONTAMINANTS</u> IN THE ENVIRONMENT

3.1 INDIVIDUAL PCB CONGENERS

The Group discussed the need for industrial CBs and the suggestions of canddidate Nos proposed by ICES. GEMSI's approach has been only to quantify CBs that are easily spearated. Of those selected by ICES only 101, 138, 180 and 44 are well defined. GEMSI would agree with the complete list of all reports published included a sample chromatogram with the data. It was also noted that 66/95 is probably 95/80. Additional peaks that GEMSI would suggest have IUPAC Nos. 26, 49, 37, 40, 61, 84, 99, 82, 183, 194, 206, 209. Those that can be separated with a good SE53 column are 15/18, 31/28, 149/118, 153/132/105, but a chromatogram should be shown. The Group noted that the recent Canadian 51 component Standard produced by NRC is very useful as it contains some of the peaks we are interested in; however, not all of those present are found in the marine environment. The Group discussed that there are different IOPAC Nos in different marine compartments (ie. water/biota/sediments) and that work should aim to resolve separation problems with different matrixes.

3.2 INDIVIDUAL CB METABOLITES

The Group discussed metabolites of CBs and the suggestion that standards need to be produced. A key to identifying CB's subject to metabolic and/or chemical degradation would be the compositional differences between the physical phases of the marine environment (atmosphere/water/ particles) and biological systems. It is proposed that this will be a part of intersessional work (Drs. Duinker and Palmork).

3.3 TOXAPHENE

There is a need for identification/quantification of individual polychlorinated camphenes occurring in the environment, and it is hoped that some of the problems can be resolved intersessionally. This is still a matter of research and development.

3.4 POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons in the environment originate mainly from contamination by fossil fuels and from pyrolysis and incomplete combustion of any material containing carbon and hydrogen. Due to the high temperature of their formation, pyrogenic PAH are unsubstituted. PAH from fossil fuels are both unsubstituted nuclei and alkylated derivatives. Characteristic components of fossil fuels which are not normally found in pyrolysis products are heterocyclic PAH containing sulphur.

The most effective analytical tool for characterizing and quantifying PAH is a combination of capillary gas chromatography and mass spectrometry. To enable the use of internal standards for quanitification, reference compounds should be chemically identical to those found in samples, but recognizable as reference ompounds. Perdeuterated PAH have these characteristics and would thus be ideal reference compounds for quantifying PAK in environmental samples.

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The following compounds are suggested:
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anthracene-D<sub>10</sub>
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phenanthrene-D₁₀

fluorene-D₁₀

pyrene-D₁₀

fluoranthene-D₁₀

acenaphthene-D₁₀

benzo(a)pyrene-D₁₂

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benzo(e)pyrene-D<sub>12</sub>
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benzo(a)anthracene-D₁₂

chrysene-D₁₂

dibenzo(b,d)thiophene-D_g

9-methylphenanthrene-D₁₂

benzo(b)naphto(2,1,d)thiophene-D₁₀

1-methylpyrene-D₁₂

1-methylchrysene-D₁₄

The Group emphasized the need for uncompromized reference materials and the need for intercalibrations.

4. <u>SEDIMENTS</u>

At the sub-group meeting in Kiel, June 1985, the Group was asked to provide input to the Manual, in preparation for the analysis of sediments as monitoring tools. These recommendations were incorporated into the Manual. However, the draft Manual was not available for comment at the time of the sub-group meeting.

5. ATMOSPHERIC SAMPLING

GEMSI should be more involved in assessing atmospheric inputs with respect to flux measurments in open ocean systems. Intersessional work at the Bermuda Biological Station had generated results for adsorbent efficiencies, breakthrough volumes, etc. which could be written into a methods manual for atmospheric sampling. Much work has been done in the past five years to develop flux models. Dr Knap suggests further subgroup work to address these aspects. There is currently no way to accurately measure dry deposition. The availbale models are very divergent. It is feasible to measure concentrations in aerosols, particles and rain. Total deposition can be measured, but fluxes are only crude estimates. It is appropriate for GEMSI to review the state-of-the art. There may be some overlap with GESAMP and ICES Working Groups, but these other groups do not seem to be moving as fast as desirable, with respect to modelling fluxes of organic contaminants. Dr Ehrhardt discussed the measurements of atmospheric depositions of UV-fluoresence material in Sahara dust where concentrations of 0.4 ug/1 in surface seawater, increased to 140 ug/l after a storm. Source dust was not high in UV-F signal. The preliminary hypothesis is that the dust may act as a scavenging mechanism causing deposition of air-borne contaminants. Dr. Knap has agreed to collate a review on the subject of atmospheric deposition for the next GEMSI session.

The Group noted that UNEP plans to produce a reference method for organics in aerosols and wet precipitation.

The Sub-Group plans to develop a position document for strategies to measure atmospheric depositions in the context of computing mass balances for organic contaminants. This report is planned for 1986.

6. PORT MORESBY WORKSHOP

The Group noted that a Manual for capillary gas chromatography for CHC's would be ready for the Workshop. A proposal to provide suitable equipment to the Workshop has been sent to UNEP and was discussed sessionally. An alternate suggestion would be to provide a contract to a key laboratory to send and insure equipment for the course. It is suggested that at least two GEMSI members be on-site during this exercise to instruct in capillary gas chromatography and interpretation of the chromatograms. The Bermuda Biological Station has been suggested as a possible laboratory to carry out this exercise. Standards are important, and it also suggested that the GEMSI members bring appropriate Standards. Dr Duinker will send a letter to Dr. Mowbray soliciting a list of compounds to be measured, what standards they have and what compounds they would like to separate.

A division of responsibilities needs to be worked out so that there is a balance between capillary and packed GCs. Dr Duinker will include these aspects in a letter to Dr. Mowbray.

7. <u>HPLC versus GC-MS</u>

The efficiencies of HPLC and GC-MS system for generating analytical data pertinent to the GIPME programme were compared in a discussion. It was recognized that many laboratories involved in GIPME have access to fluorimeters which, in combination with a basic HPLC separation unit, can be used to detect material in column cffluents which either IOC/GGE(MSI)-VII/3 Annex IV - page 8

fluoresce themselves or can be converted into fluorescent derivatives. Although this technique may be useful for sensitive detection of, for example, individual PAHs, a GC-MS system offers considerably more flexibility and is the only analytical instrument capable of unequivocal identification of organic contaminants or ultratrce levels. No unanimous conclusion was reached, but it may be appropriate to make laboratories having fluorimeters aware of their potential use as detectors in HPLC systems.

8. RIVER INTERCOMPARISON EXERCISE - THAILAND

- 8.1 ORGANICS SECTION
- 8.1.1 Introduction

There is, at present, little information available on the transport mechanisms, seasonality and amounts of organic contaminants by rivers. The methods that are currently employed for contamination assessment of natural waters are mainly designed for seawater, and therefore factors such as suspended and colloidal material, pH regime, etc, that need to be considered in river studies, provide a more difficult matrix. Phase separation (filtration/centrifugation) may be an essential component of any contamination assessment of a river, which is in contrast to some methods currently used for seawater (IOC Manuals and Guides 13). The relationship of adsorption/desoprtion mechanisms involved in colloidal, dissolved/dispersed, particulate interactions may be different in the pH regime provided by rivers than in the open ocean. The relationship between DOC/POC and other natural organic compounds such as fulvic acid and contaminant occurrence has not been studied. It could have a relationship enabling prediction of contaminant occurrence.

Compounds with different solubilities and octanol/water partitioning coefficients are partitioned differently between particulate and dissolved phases. For example, Lindane (trans-hexachlorocyclohexane) appears to exist mainly in the dissolved phase whereas some PCB congeners are more prevalent in the particulate phase. The study of some of these synthetic compounds could lead to a development of marker compounds that could be used to identify mechanisms of river discharge and mixing in the coastal zone.

There are also very few high resolution data on the occurrence and concentration of contaminants in these rivers.

8.1.2 Goals

The main goal of the organic section of the proposed workshop is to train scientists from the region in contamination assessment. The main priorities are to be the following:

- (i) to test Manual and Guides N° 13 to detect Hot Spots in a river;
- to investigate the intercomparability of analyses of a homogenized river sample;
- (iii) whether it is possible to assess spatial and temporal variability of fluoresence intensity;
- (iv) to investigate phase distribution of some of the fluoesence intensity;

- (v) an inventory of contaminant compounds in the contaminated Chao Phraya River;
- (vi) a relationship between some natural and synthetic compounds.

The Group agreed with these goals and designed a set of experiments that would fulfil them. It was also agreed that there would be 10 participants in the organics section with a high proportion of GEMSI members, in order to maximize the experiment. Some of these funds for participation will be available from TEMA. Dr. Dawson also outlined other budgetary aspects of the meeting.

9. OTHER ITEMS

9.1 DISCUSSION ON ORGANICS IN OPEN OCEAN BASELINE PROGRAMME

Since the methodology to measure individual organic contaminants in open ocean seawater is still in the research and development stage, it cannot be recommended that organics be included in an open ocean baseline scheme as currently planned for inorganic contaminants. However, enough progress has been made on the development of sampling techniques for open ocean surface seawater, on the instrumental identification of selected organic contaminants and on the understanding of the bioceochemical cycling of organic contaminants in the marine environment; the Sub-Group was thus able to offer the following suggestions at this stage for the introduction of a baseline monitoring programme for selected organics:

Techniques developed for sampling the low concentration of organic contaminants in seawater rely on the extraction of large volumes seawater. The required flow rates for quantitative extraction, coupled with the need to determine the variability inherent in the sampling method makes it essential that initial tests be conducted at one, or a few, well hydrographically characterized stations. Much uncertainty exists on the accuracy of all previous measurements of components such as PCB's in open ocean water. Thus, the major initial aim of a bseline study should be the evaluation of large volume techniques to produce accurate values for selcted components. Flux studies using sediment traps over long time periods have successfully shown that the residence times of many organic contaminants in surface waters are relatively short (to the order of a few months to years) due to sedimentation processes. It is also true that in open sea conditions, atmospheric transport and deposition act as major sources of many organic contaminants. Since this input can be removed relatively rapidly from surface waters, measurements of ambient concentrations will fluctuate both on the basis of input rates and as a result of the rate of sedimentation, degradation and other removal processes. It was also pointed out that most organic contaminants have been released into the global environment in the time scale of the last 50 years. As a result, fluxes would be difficult to estimate from sedimentary records in basins of slow sedimentation rate. Thus estimates of current vertical fluxes through the oceans using sediment traps and/or large volume suspended particulate analysis should complement measures of ambient surface water concentrations for components generally adsorbed to particles, such as PCB's. Other componenets, such as the HCH isomers occur mostly in the dissolved state, but even to establish a baseline concentration for one ocean site, would have to be made over at least a yearly cycle.

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9.2 REACTION PRODUCTS

Water soluble reaction products formed by photo-oxidation processes appear to increase the toxicity of spilled petroleum oils. This phenomenon has been demonstrated by LD_{60} tests and in enclosed ecosystem experiments. It would thus be appropriate for this Sub-Group to review methods for the determination of reaction products as already suggested in our last report. Dr Ehrhardt described results obtained by the Kiel Laboratory in isolating reaction products from individual hydrocarbons, such alkyl benzenes and n-alkanes (Ehrhardt and Petrick, 1984 and 1985). He noted that polar reaction products can be extractd from seawater with XAD-2 or XAD-4 resins. In laboratory experiments, he has seen the appearance of mono- and -diketones, alkenes and aldehyes and secondary alcohols. His strategy has been to identify the products generated from a precursor hydrocarbon and then to look for these products in the environment. The Group noted that, by using this approach, even if the precursor molecules are not the most toxic, their analysis may still provide some estimate for what more toxic reaction products could be expected in 1985 and continuing into the future.

Tremendous problems in preparative chemistry and analysis remain to be solved. And there is still much uncertainty in distinguishing from anthropogenic compounds. Thus the Group felt that the stage has not yet been reached when methods could be recommended, but it would be a useful exercise to summarize the knowledge of methods available within the Group. This area should be given high priority. It represents a major new direction to be taken in 1986 for the Sub-Group on the Analysis of Individual Organic Contaminants. The Group noted that reaction product chemistry is extremely relevant to air/sea exchange studies and to studies on global fluxes.

9.3 HIGH FAT SAMPLES AND POLAR CONTAMINANTS

Extension of the analysis of polar contaminants and reaction products to organisms depends on the development of methods for separating biogenic lipids. Dr Burns contributed a background paper demonstrating the potential of HPLC methods to extend analytical capabilities to more polar contaminants for high fat samples.

Dr Duinker suggested that the Sub-Group formulate a series of questions for GEEP to formulate priorities for developing methods for expanded classes of compounds to monitor. Due to the extreme difficulty of complete characterization of reaction products, it may be feasible to base toxicity assessment on a combination of analytical chemistry and toxicity studies.

9.4 SEAWATER

As a part of the Group's continuing efforts to solve problems related to the analysis of trace organic contaminants in sewater, Dr Ehrhardt contributed a method sheet for cleaning silica gel.

Discussion on the effects of acidification on the extraction efficiency of hexane for removing hydrocarbons in seawater revolved around the behaviour of colloids in binding organic contaminants. Further work should strive to increase the understanding of the binding of organic contaminants to particles and colloids.

ANNEX V

SESSIONAL REPORT OF SUBGROUP ON THE MUSSELWATCH QUESTIONNAIRE

The Sub-Group examined the draft questionnaire that had been prepared intersessionally by Dr.Topping. They agreed to a number of modifications to the questionnaire in terms of format, style and content and Dr. Topping agreed to incorporate these changes and the suggestions made in writing by other members of GEMSI in the final version. The final questionnaire is to be sent to IOC/UNEP early in 1986 for distribution to Regional Seas representatives. The Chairman would also be sending copies to Dr Calder (NOAA) for distribution to US laboratories and to representatives in ICES laboratories. A preliminary report on the responses to the questionnaire will be prepared for submission to the next session of WC GIPME. This report would also be tabled for discussion at the next session of GEMSI.

ANNEX VI <u>SESSIONAL REPORT OF SUBGROUP ON</u> RIVER INPUT OF POLLUTANTS

1. INTERSESSIONAL ACTIVITIES

During the meeting of GEMSI VI in Woods Hole, the Sub-Group prepared a questionnaire to be circulated to potential participants of the proposed River Input of Pollutants Intercalibration Exercise so that their comments, interests and experiences could be taken into account when formulating the final Workshop design. This questionnaire was sent out by the Chairman of the Sub-Group during December 1984.

The Sub-Group Chairman met with the local steering committee for the proposed exercise in Thailand during January 1985, while he was there to participate in a cooperative research programme. The purpose of this meeting was to discuss various logistical aspect of the proposed exercise with representatives of cooperating agencies in Thailand. Dr Manuwadi Hungspreugs acts as chairperson for this group and also provides overall liaison for GEMSI in Thailand.

Finally, five members of the Sub-Group on River Inputs met in Bangkok from 22 to 26 April 1985, to develop detailed plans for the exercise incorporating results of the questionnaire. The Group was chosen to give balance to both the organic and inorganic aspects of the design and logistics of the exercise.

From the responses to questionnaires sent to key agencies, institutions and individuals, it appears that participants from regional laboratories have some experience in river studies and are interested in participating in both inorganic (ie. trace metals) and organic aspects of the proposed exercise. For this reason, it is recommended that participation from regional laboratories be limited to about 12. Based on the responses to the questionnaires thus far this number will probably allow for adequate regional participation. There will probably be six participating core laboratories.

The proposed exercise will be in the form of a workshop having the following three components:

- 1. Classroom discussions/demonstrations
- 2. Experiments
- 3. Intercalibration of analyses

The first two components will provide the training part of the exercise. This will include classroom lectures and discussions on past experiences with intercalibration exercises (eg. PANCAL), the basis and need for a river intercalibration exercise, general aspects of river transport of pollutants (eg. hydrology, estuarine mixing, inhomogeneity, etc) and potential problems of sampling and analysis. Demonstrations of sampling and analytical techniques will be provided to give participants "hands on" experience. Participants will also be involved in experiments designed to address some fundamental problems associated with river transport studies. IOC/GGE(MSI)-VII/3 Annex VI - page 2

For the intercalibration component, the participants will be involved in collecting and preparing samples to be returned to their home laboratories for pollutant analysis. Some analyses, however, will be performed during the Workshop as well.

2. <u>SESSIONAL ACTIVITIES</u>

The Sub-Group met sessionally to discuss the details of dayto-day activities during the proposed Workshar. For this purpose, an organic and an inorganic group met separately. The results of their deliberations were combined by the Sub-Group and will be included in a Workshop Prospectus by the Chairman during the next two months. This Prospectus will then be available for mailing to individual laboratories who will be invited to particpate.

During the sessional period, the Sub-Group also considered the cost of conducting the Workshop and submitted proposals for the consideration of the IOC Secretariat.

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ANNEX VII

SESSIONAL REPORT OF SUBGROUP ON REFERENCE MATERIALS

The group first agreed to deal with the content of the reports IOC/GGE(MSI)VII/12 and IOC/GGE(MSI)VII/13, and then the recommendations arising from these reports.

There was general acceptance of the contents of the two reports, realizing that document IOC/GGE(MSI)VII/13 (the Washington sub-group meeting report) takes precedence over and supersedes document IOC/GGE(MSI) VII/12 (the Geneva sub-group report). It was consequently agreed that Drs. Walton and Andersen would undertake editorial and typing corrections to the present draft of the Washington meeting report for use at the IOC Assembly. Dr. Walton would be pleased to receive suggestions for correction/improvement from GEMSI members before the close of GEMSI VII.

The sub-group then dealt with the recommendations and future action in respect to marine reference materials. Recommendation 2 IOC/GGE(MSI)VII/13 for the preparation of an up-to-date publication on reference materials was wholly supported by the group. The offer, made by Dr. Calder of the US/NOAA, to prepare a catalogue of available reference materials was noted and enthusiastically accepted. Some discussion of the content and nature of the publication then ensued. In summary, it was agreed (1) that this publication should be as comprehensive as possible and that it would include reference materials for radioactive, physical chemical and stable isotopic components; (2) that representatives of producing agencies (e.g., NIES, BCR, ICES) should be solicited for information through correspondence; and (3) that the catalogue would extend to materials that, although primarily for geological or other non-marine applications, might be used by the marine community. It was further agreed that only materials available in quantities to supply at least 100 users would be catalogued. This would enable a discussion to be made about the inclusion of previously used uncompromised reference materials (such as those used in previous ICES and ICES/SCOR intercomparison exercises).

The group then turned to the matter of definitions to be used in the catalogue for the categorization of materials. It was agreed that the definitions contained in the report of the ICES Marine Chemistry Working Group would be used as a starting point but that Dr. S. Berman (N.R.C., Canada) should be approached by correspondence to provide an authoritative list of categories and definitions for reference materials. This would form part of the initial preface material to the catalogue and would be used to categorize materials listed in the catalogue. Similarly, it was recognized that there was a need to identify, and discriminate between, the different certification procedures used for standard reference materials. It was therefore agreed that information on the certification procedures used by the producing agencies would be sought at the same time as information on products. Dr. Calder believed it would be possible to produce a first draft of the catalogue within the next few months and it was accepted that this would form the starting point from which the catalogue would be updated, extended, and refinements made to the manner in which materials were categorized. The catalogue would initially be a USA/NOAA product but

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the subsequent updating and distribution etc. could be handled through other agencies as appropriate. The comments of producers would be requested in respect to format and presentation of materials in the catalogue and the first edition would be sent to all members of the GEMSI intersessional sub-group for comments before submission to IOC and UNEP.

The sub-group then turned to the other recommendations in VII/13. Recommendation 5 advocates that ISO/REMCO be informed of GEMSI activities vis-à-vis standards and reference materials. It was agreed that IOC (Dr. Kullenberg) be requested to inform ISO/REMCO by letter of these activities for information purposes.

Recommendations 1, 3 and 4 of the sub-group report (VII/13) are interrelated and deal with future activities in respect to marine standards It was agreed that the meetings of the combined group of within GEMSI. users (marine community users) and producers should continue as a vehicle to: (1) identify suitable reference materials being made available; (2) identify unsatisfied requirements in relation to marine contamination and pollution studies; (3) set priorities for the production of needed reference materials; (4) identify potential sources of such materials; (5) solicit appropriate producers to prepare these materials; and, (6) develop mechanisms for notification and distribution of marine reference This group should comprise representamaterials to the extent required. tives of three types: users, producers and agencies. The users should comprise experts in:

- marine sediments
- biological tissues
- seawater
- inorganic marine chemistry
- organic marine chemistry.

The agencies <u>inter alia</u> that might be represented in the group, or nominate representatives, are UNEP, IOC, IAEA, ICES and FAO. The producers would include those agencies already identified as producing reference materials for more applications and any other agencies in a position to assist in the preparation of such materials.

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SESSIONAL REPORT OF THE SUBGROUP ON THE DESIGN OF AN OPEN-OCEAN BASELINE SURVEY FOR TRACE METALS IN THE ATLANTIC OCEAN

The Group began its deliberations by reviewing the paper in detail and offering Dr. Bewers some suggestions for its revision. The Group accepted the justification of the survey and felt that its successful completion would be very valuable.

The Group agreed on the locations proposed for the deep ocean stations (subject to the agreement of Dr. Blanton as the physical oceanographer involved) and the importance of using stations some distance from the water mass formation areas was emphasized. This strategy should overcome problems arising from the erratic nature of water mass formation. This was recognized as a particular problem in the South Atlantic where the stations have been sited north of the convergence zones.

The Group suggested that the role of the transects, in describing the major ocean currents and in studying water mass formation areas in detail, be clarified. It was recognized that the question of possible seasonality needs to be considered and it was noted that the exact route of the transects is not critical. The discussion of the monitoring strategy highlighted some problems and it was concluded that this section should not be considered within this baseline survey.

The Group then turned to discussion of the implementation of the programme. An extended list of elements was prepared and it was felt that laboratories with demonstrated competence for these elements would probably agree to analyze the samples, provided they were satisfied with the sample collection procedures.

The value of archiving samples was discussed and it was concluded that this was logical, though past experience with archived samples suggested they may not be extensively used. The question of filtration of samples was raised and it was concluded that unfiltered samples would probably be acceptable, but that separate determinations of dissolved and particulate concentrations on some samples would be useful. It was also decided that only routine hydrographic parameters and nutrient concentrations need to be determined on the samples though ²¹⁰Pb and freon determinations would be useful for the transects and the deep water, respectively.

Dr. Bewers offered the view that the logistic of the sampling would be simplified by using only 2 ships, one probably for the South Atlantic and one for the North Atlantic. It was felt that the ships for this work could be made available. The Group recognized the scale and critical importance of the task of sample collection and some of the groups competent to carry out this work were identified (see list below). IOC/GGE(MSI)-VII/3 Annex VIII - page 2

The Group concluded that the proposed project is important and logistically feasible. Dr. Bewers then undertook to incorporate the Group's suggestions into a revised paper which he would then send to various groups with demonstrated competence in this field asking for expressions of interest in the sample collection and analysis programmes. Dr. Bewers expressed the hope that this process could be completed within 3 months.

List of inter alia laboratories competent to collect the samples

| Name | Institute | Country |
|----------------|-------------------|---------|
| Bacon | WHOI | USA |
| Boyle | MIT | USA |
| Burton/Statham | Univ. Southampton | UK |
| Flegal | Univ. California | USA |
| Kremling | Kiel | FRG |
| Olafsson | Univ. Reykavik | Iceland |
| Rowland | Univ. California | USA |
| Westerlund | Gottenburg | Sweden |
| Yeats | BIO | Canada |

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ANNEX IX

TIMETABLE OF GIPME ACTIVITIES

| ACTIVITY | LOCATION | DATE | GEMSI INVOLVEMENT | AGENCY |
|--|--------------------------------------|-------------------------|--|--------------|
| Petroleum Hydrocarbons Symposium | Mayaguez, Puerto Rico | Dec.1985 | Dawson Albaiges | IOC |
| GEEP-II | Paris, France | Dec.1985 | Palmork | IOC |
| IOC Executive Council | Paris, France | Mar.1986 | Andersen | IOC |
| River Inputs Workshop | Bangkok, Thailand | April/May 1986 | Windom, et. al. | IOC |
| WESTPAC 2nd Trace Metal Intercalibra- tion | Distribution from ILMR, Monaco | late 1985 early 1986 | Aston,Topping Regional Co-ordinators | IOC/ UNEP |
| Mediterranean Petroleum Hydro- carbon Workshop | Barcelona, Spain | Sept,1986 | Albaiges | 10C/ UNEP |
| Organochlorines Workshop | Port Moresby Papua New Guinea | June/July 1986 | Uthe Duinker Knap | IOC/UNEP |
| Intercalibration Workshop, CPPS | Quito, Ecuador | 1986/1987 | Albaiges Bottello | IOC/ UNEP |
| Petroleum Hydrocarbons Musselwatch Workshop | Cancún, Mexico | Oct./Nov. 1986 | Atwood Albaiges Bottello | IOC/UNEP |
| Biological Effects Workshop | Oslo, Norway | Oct./Nov. 1986 | representa- tive | IOC |
| Pre-GIPME Symposium | Paris, France | Oct./Nov. 1986 | •• | 100 |
| WC-GIPME VI | Paris, France | Sept/Oct 1986 | Andersen, Duinker | IOC |
| GOPPS-IV | Paris, France | Oct. 1986 | Andersen, Duinker | IOC |

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ANNEX X

PROPOSAL FOR EQUIPMENT SUPPLIES TO REGIONAL PROGRAMMES

PREAMBLE

In the event that funds are available in UNEP for the provision of equipment for Joint Agency activities scheduled for 1986 and the extension of programmes beyond, GEMSI, at its Seventh Session, has reviewed the current status of preparation for joint IOC-UNEP training workshops and intercalibrations and has reached the conclusion that the following regional programmes and identified research institutions would benefit from an early provision of equipment.

The proposals are ordered according to the priorities assigned by GEMSI:

COBSEA/WESTPAC - CO-OPERATION

The Department of Marine Chemistry of Chulalongkorn University (Bangkok, Thailand) has been an active participant in all previous intercalibration and major global programmes including the initiation of Musselwatch activities and the monitoring of petroleum residues in the Upper Gulf of Thailand and the Andaman Sea.

The Department is also instrumental in the conduct of a major study/ intercalibration of riverine inputs.

The Department has further committed a major portion of its resources for 1986 to the provision of capillary GC for participation in the Organochlorine Programme of the COBSEA Programme.

It is proposed that the necessary capillary GC and integrator, with supplies and an HPLC be supplied to this institute to enable it to serve a function as an advanced centre for teaching and intercalibration.

| Total | cost: | US\$ | 22,100 | GC |
|-------|-------|------|--------|------|
| | | | 20,000 | HPLC |

SPREP/WESTPAC - CO-OPERATION

In view of the scheduled Organochlorine Workshop in Papua New Guinea (Port Moresby, June-July 1986) and the agreements reached between IOC, UNEP and their Group of Experts, GEMSI, to provide manuals, instruction and equipment for capillary gas chromatographic techniques, it is proposed that a capillary GC and integrator, and supplies (US\$ 22,000) be provided to the Biology Department, c/o Dr, D. Mowbray, University of Papua New Guinea.

CAP/IOCARIBE - CO-OPERATION

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Following the IOC-UNEP Training Workshop on Petroleum Hydrocarbon Monitoring in the Caribbean, scheduled for October 1986 in Cancún, Puerto Morelos, Mexico, a number of proposals have been generated to ensure an adequate follow-up and an initiation of a network of laboratories to contribute to a Musselwatch for the Caribbean. Recognizing that an imbalance exists between institutes in terms of available equipment for initiating these activiites, early attention to meeting these needs appears warranted. As a result, the following is recommended: IOC/GGE(MSI)-VII/3 Annex X - page 2

- Provision of a capillary GC (US\$22,000) to the University of Costa Rica. Dr. Alfonso Mata, as an institute director, has already been actively involved in petroleum monitoring and the provision of training opportunities.
- Provision of a capillary GC (US\$22,000) to the Cargagena institute in Colombia where major efforts in training and monitoring have been made.
- Provintion of a spectrofluorometer (US\$25,000) to the University of Mayaguez, Puerto Rica to enable the laboratory to continue to function as a training and intercalibration centre.
- Provision of an HPLC facility (US\$20,000) to the Universidad Naçional Autonoma de Mexico for use in the Workshop to Determine PAH's in Sediment and Organisms.

ENHANCED CO-OPERATION IN CPPS

Early attention should be paid to the provision of equipment for the training workshop in CPPS involving 15 laboratories, scheduled for mid-1986 in Quito.

Until the results of consultant missions identify substantial gaps in key laboratories, it is estimated that an atomic obsorption spectrophotometer, a capillary gas chromatograph and a spectrofluorometer would be required by three laboratories with the suggestion that these would be available for future training and intercalibration workshops.

Costs

| AAS t | US\$ 40,000 |
|--------------------|-------------|
| Spectrofluorometer | 25,000 |
| Gas Chromatograph | 22,000 |

ANNEX XI

STATUS OF REFERENCE METHODS FOR MARINE POLLUTION STUDIES November 1985

A. Sanitary quality of coastal recreational and shellfish-growing waters

| No. 1 | UNEP/WHO: Guidelines for monitoring the quality of coastal recreational and shellfish-growing waters. | draft(E) 09.05.84 |
|--------|--|--|
| No. 2 | UNEP/WHO: Determination of total coliforms in sea water by the membrane filtration culture method. | Rev.1(E) 31.08.83 Rev.1(F) 31.10.83 |
| No. 3 | UNEP/WHO: Determination of faecal coliforms in sea water by the membrane filtration culture method. | Rev.1(E) 31.08.83 Rev.1(F) 31.10.83 |
| No. 4 | UNEP/WHO: Determination of faecal strepto- cocci in sea water by the membrane filtration culture method | Rev.1(E) 31.08.83 Rev.1(F) 31.10.83 |
| No. 5 | UNEP/WHO: Determination of faecal coliforms in bivalves by multiple test tube method. | Rev.1(E) 31.08.83 Rev.1(F) 31.10.83 |
| No. 21 | UNEP/WHO/IAEA: Determination of total coliforms in sea water by multiple test tube (MPN) method. | draft(E) 19.07.85 |
| No. 22 | UNEP/WHO/IAEA: Determination of faecal coliforms in sea water by multiple test tube (MPN) method. | draft(E) 19.07.85 |
| No. 23 | UNEP/WHO/IAEA: Determination of faecal streptococci in sea water by multiple test tube (MPN) method. | draft(E) 19.07.85 |
| No. 28 | UNEP/NHO/IAEA: Determination of staphy- lococcus aureus in sea water and sewage by the membrane filtration culture method. | in preparation |
| No. 29 | UNEP/WHO/IAEA: Determination of pseudomonas aeruginosa in sea-water and sewage by the membrane filtration culture method. | in preparation |
| No. 30 | UNEP/WHO/IAEA: Isolation/enumeration of salmonella from sea water and sewage. | in preparation |
| D | UNEP/WHO/IAEA: Determination of faecal coliforms in estuarine waters, suspended matter and sediments. | in preparation |
| M | UNEP/WHO/IAEA: Statistical methods for the evaluation of results from monitoring the quality of constal reactional and shellfish- growing waters. | in preparation |

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- B <u>Chemical contaminants in marine organisms</u>
 - No. 6 UNEP/FAO/IAEA: Guidelines for monitoring in preparation chemical contaminants in marine organisms. No. 7 UNEP/FAO/IOC/IAEA/: Sampling of selected Rev.2(E) 12.11.84 marine organisms and sample preparation for trace metal analysis. No. 8 UN&P/FAO/IOC/IABA/: Determination of total Rev.1(E) 12.11.84 mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry. No. 9 UNEP/FAO/IAEA: Determination of total draft(E) 22.04.85 arsenic in selected marine organisms by hydride generation atomic absorption spectro -photometry. No. 10 UNEP/FAO/IABA: Determination of total (E) 12.11.84 selenium in selected marine organisms by hydride generation atomic absorption spectrophotometry. No. 11 UNEP/FAO/IOC/IAEA/: Determination of total Rev.1(E) 12.11.84 cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry. No. 12 UNEP/FAO/IAEA: Sampling of selected marine Rev.1(E) 12.11.84 organisms and sample preparation for the analysis of chlorinated hydrocarbons. No. 13 UNEP/FAO/IAEA: Determination of methyl-(E) 12.11.84 mercury in selected marine organisms by gas chromatography. No. 14 UNEP/FAO/IOC/IABA: Determination of DDTs in preparation and PCBs in selected marine organisms by packed column gas chromatography. No. N UNEP/FAO/IOC/IABA: Determination of DDTs in preparation and PCBs in selected marine organisms by capillary column gas chromatography.

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- C. <u>Chemical contaminents in sea water</u>
 - No. 16 UNEP/IAEA: Determination of DDTs, PCBs, draft(E) 21.09.82 PCCs and other hydrocarbons in sea water by gas chromatography.
 - No. 18 UNEP/IOC: Determination of total draft(E) 16.09.83 dissolved cadmium in sea water by differential pulse anodic stripping voltammetry.
 - B UNEP/IOC/IAEA: Monitoring of petroleum in preparation hydrocarbons in sea water.
- D. Chemical contaminants in marine sediments and suspended matter
 - No. 17 UNEP/IAEA: Determination of DDTs, PCBs, PCCs draft(E) 22.09.82 and other hydrocarbons in marine sediments by gas-liquid chromatography.
 - No. 20 UNEP/IOC: Monitoring of petroleum hydro- in preparation carbons in sediments.
 - No. 26 UNEP/IAEA: Determination of total mercury draft(E) 25.03.85 in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry.
 - No. 27 UNEP/IABA: Determination of total cadmium draft(E) 25.03.85 in marine sediments by flameless atomic absorption spectrophotometry.
 - No. 31 UNEP/IAEA: Determination of total chromium draft(E) 17.07.85 in marine sediments by flameless atomic absorption spectrophotometry.
 - No. 32 UNEP/IARA: Determination of total cobalt draft(E) 17.07.85 in marine sediments by flameleas atomic absorption spectrophotometry.
 - No. 33 UNEP/IAEA: Determination of total copper draft(E) 17.07.85 in marine sediments by flameless atomic absorption spectrophotometry.
 - No. 34 UNEP/IAEA: Determination of total lead draft(E) 17.07.85 in marine sediments by flameless atomic absorption spectrophotometry.
 - No. 35 UNEP/IAEA: Determination of total nickel draft(E) 17.07.85 in marine sediments by flameless atomic absorption spectrophotometry.
 - No. 36 UNEP/IAEA: Determination of total vanadium draft(E) 17.07.85 in marine sediments by flameless atomic absorption spectrophotometry.
 - **E** UNEP/WHO/IAEA: Determination of phosphorus in preparation in suspended matter and sediments.

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F UNEP/WHO/IAEA: Determination of nitrogen in in preparation suspended matter and sediments.

E. Chemical contaminants in estuarine waters and suspended matter

| No. 19 | UNEP/IOC/IAEA: Determination of total mercury in estuarine waters and suspended sediment by cold vapour atomic absorption spectrophotometry. | draft(E) 25.03.85 |
|--------|---|-------------------|
| C | UNEP/IARA: Guidelines for monitoring of estuarine waters and suspended matter. | in preparation |
| R | UNKP/WHO/IABA: Determination of total phosphorus in suspended matter and sediments. | in preparation |
| F | UNEP/WHO/IAEA: Determination of totel nitrogen in suspended matter and sediments. | in preparation |
| G | UNEP/WHO/IAEA: Determination of BOD5 and COD in estuarine waters. | in preparation |
| I | UNEP/IOC/IABA: Determination of total cadmium in estuarine waters and suspended matter. | in preparation |

F. Chemical contaminants on beaches

No. 15 UNEP/IOC/IAEA: Monitoring of tar on marine draft(E) 25.03.85 beaches.

G. <u>Atmospheric chemical contaminants</u>

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- No. 24 UNEP/WMO/IAEA: Sampling of aerosols and draft(E) 12.04.85 wet precipitation for analysis of chemical pollutants.
 0 UNEP/IAEA: Determination of selected trace in preparation metals in aerosols and in wet precipitation.
 P UNEP/IAEA: Determination of halogenated in preparation hydrocarbons in aerosols and in wet precipitation.
- Q UNEP/WMO/IAEA: Sampling of dry deposition. in preparation

H. <u>Effects on marine organisms and ecosystems</u>

No. 25 SPC/UNEP: Coral reef monitoring handbook. (E) 27.08.84

- A UNKP: Sampling and identification of common in preparation Mediterranean Scyphomedusae and evaluation of their occurrence.
- H UNEP/FAO/IAEA: Acute biological toxicity in preparation tests.
- J UNEP/FAO/IAEA: Biological non-acute in preparation toxicity tests.

I. Standard physical, chemical and meteorological observations

- K UNEP/IOC/IAEA: Determination of basic ocean- in preparation ographic and meteorological conditions.
- L UNEP/IOC/IABA: Determination of standard in preparation physical and chemical parameters.

J. <u>Miscellaneous methods</u>

- AD UNEP/WHO/IAEA: Determination of methyl- in preparation mercury, total mercury and selenium in human hair.
- AE UNEP/WHO/IAEA: Guidelines for monitoring and in preparation epidemiological studies on health effects of methylmercury.

ANNEX XII

SESSIONAL AD HOC SUB-GROUP ON REGIONAL MASS BALANCE REPORT

CALCULATIONS

During discussion of Agenda Item 8.4, it was suggested that the results of the MEDPOL Programme might be used to evaluate the adequacy of an existing data base for the purpose of regional mass balance calculations. GEMSI members agreed that this was possible but that it would require a detailed review of the existing data and therefore could not be accomplished sessionally. The members, however, did feel that characteristics of a data base that make it suitable for mass balance calculations could be generically outlined sessionally and an <u>ad hoc</u> group was therefore formed for this purpose. The views of this group are summarized below.

Mass balance calculations are based on input and output budget estimates and depend on assumptions made about the system regarding the degree to which it is in steady state. The major discussions of the group focussed primarily on the requirements of the data base for making budget estimates. The following were felt to be the most important:

1. The success of any mass balance calculation for a pollutant in a system will depend on the ability to establish water and sediment balances. Therefore, it is important that the fluxes of the phases which carry the pollutant be as accurately and precisely known as possible. For example, gauging records for all rivers delivering material to the system should be available over a long period of time to allow for estimating annual discharges and major temporal variations, in discharges. Likewise, sufficient information on annual rainfall and its regional variability must be available. For the purpose of estimating rates of sediment removal from the system, sedimentation rates and their regional variability must be known. More contemporary budget estimates (i.e., steady state not assumed over recent time) will require knowledge of particle removal rates based on sediment trap data.

2. Concentrations of the pollutant for which budget estimates are being made must be adequately characterized in the input and removal phases. Major temporal variations in pollutant concentrations must be understood in relation to temporal variations in the fluxes of the carrier phases.

3. All sources of direct inputs to the system due to such things as pipeline discharges, dumping, etc., must be quantified.

4. Data from all sources (i.e., participating laboratories) providing inputs to the data base must be comparable in accuracy and precision. Assessment of this should be based on laboratory intercomparison exercises including the analysis of uncompromised reference materials.

MEDITERRANEAN SEA : OBJECT - DATA

Various sets of data can be obtained through a literature search, and through the MEDPOL database and measurements made in various countries in the region. Only organics ware considered.

COMMENT ON THE ORGANICS

From a literature search conducted by Dr. Dou, it is clear that broad areas are not sufficiently documented for dry depositions, wet depositions, and atmospheric concentrations of pollutants such as Hydrocarbons, PAH's, Chlorinated HC. It appears that for the organic concentrations in the organisms, sediments and water, the data will be sufficient.

Data concerning river input are difficult to obtain since they are related to the industrial contamination, which appears mainly in the estuaries. Some data have been published, but they are mainly concerned with trace metals. Other data can be obtained from country agencies.

Data concerning the output from the sea are rare, and they are mainly concerned with the oceanographic campaign PHYCEMED, or the drift to the coast of surface film by the wind.

Data concerning input by sewage have to be related to the amount of pollution per capita, since sewage treatment is rare (e.g., more in Marseille, Naples, etc. ...).

Boat released HC are important. They exist in spite of recommendations and regulations. They can be obtained from the ROCC (Malta).

Data concerning the amount of tar balls can be obtained from national agencies, mainly in Spain, France, Italy.

OBTAINING THE DATA

Three ways are possible

1. Get in touch, after an analysis, with the main laboratories, working on a scientific point of view on this question, and as for various sets of publications or data.

2. Make official contact with the various agencies of the surrounding countries, and ask for sets of representative data.

3. Obtain from the MEDPOL database, the information concerning some values. But, in this case it is not clear to whom the data belong, and if new data are directly put into the database by MEDPOL, or if the new data are coming through surrounding country agencies.

METEOROLOGICAL MODELS

Some models exist already; they have been developed by the laboratories working on trace metals and they are available.

CONCLUSION

The data concerning the Mediterranean Sea have to be gathered intersessionally. The need for IOC-UNEP recommendation is very important for the official contact with the various agencies. The need for a responsible person to have a minimum of means to conduct the work is necessary.

ANNEX XIII

SESSIONAL REPORT OF THE SUBGROUP ON QUALITY ASSURANCE

The Subgroup discussed the framework and content of a leaflet on good labroatory practice for IOC and UNEP regional laboratories which would cover the key elements of quality assurance work. Comments and suggestions for improvement were made on a list of key points drawn up by the Chairman of the Subgroup (see Table 1) and it was agreed that a revised version should be prepared intersessionally by GEMSI for the IOC and UNEP Secretariats for subsequent distribution to regional laboratories. Dr. Topping volunteered to do this taks with the assistance of some of his colleagues in GEMSI. This work would be carried out by correspondence.

TABLE 1

GENERAL GUIDANCE FOR GOOD LABORATORY PRACTICES IN RELATION TO THE COLLECTION AND ANALYSIS OF MARINE SAMPLES

| Key elements | Details |
|---------------------|---|
| Aims and Objectives | Each study should be coducted in response to clearly stated aims. Participating labo- ratories should plan and design the work to be done (ie. objectives) so that the aims are accomplished. |
| Sampling Strategy | Sampling programmes should be given careful consideration, since unrepresentative samples will lead to poor data for the purposes of the aims of the programme. Matters such as sample location, sampling frequency, sample |

type, numbers of samples, statistical

requirements for replicaiton and collection procedures should all be considered in the sampling design in order to obtain relevant and representative samples of the medium under examination from a geographical and ۶.

Sample Pretreatment Care should be taken in the handling of samples to ensure that contamination is avoided and that losses of analyte are kept to a minimum. Procedural blanks should be processed in the same way as samples, to check on contamination and "spiked" samples should be processed to assess losses during this procedure. Dissection of organisms should be carried out with knives which do not contaminate soft tissue eg. in most cases stainless steel implements can be used. (Note that slight contamination may be experienced in samples examined for trace metal content). Titanium knives may be used for the most careful work.

temporal viewpoint.

Staff The laboratory facilities should be planned Laboratory Accommodation Equipment being conducted so that the contamination of samples during the processing and analytical stage is minimized. The analytical instrumentation should be well maintained and serviced to ensure optimum performance. Staff should have appropriate experience and training in the analysis in question. Participation in workshops should be encouraged and, where

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| | Details |
|--|--|
| <u>Key elements</u> Staff Laboratory Accommodation Equipment (cont) | appropriate, visits to experts' laboratories should be arranged in order to gain additional experience and expertise. Finally, and most important analysts should be encouraged to be involved in all aspects of the work, including the assessment and interpretation of field data thereby ensuring a committment to the pro- duction of reliable data. |
| Storage of Samples | Following collection of samples, they should be stored in suitable containers which do not permit contamination or allow losses of the analyte under examination. If samples are to be stored for long periods prior to analysis, the storage procedure should be checked to en- sure that the sample does not change during storage. |
| Analytical Procedure | The method chosen for the analysis of samples must have the required sensitivity and level of detection to meet the needs of the analytical programme. As a general rule, the limit of detection should be 1/10th of the lowest con- centration that is considered might be present in field samples. The estimation of accuracy and precision of the analytical method should be done on a standard or certified reference material of appropriate matrix and analyte con- centration, i.e. the reference material should be made from the sort of material which the laboratory is going to investigate, and it must have analyte concentrations which are similar to those occurring in these natural samples. |
| Quality Control | Throughout the period of analytical work (which may last months or years) regular checks of accuracy and precision should be made to en- sure that the quality of analysis remains reasonably constant. As an additional check on analytical performance, the analysts should be encouraged to participate in interlaboratory comparisons with other laboratories in their region/country, or as part of a national or international exercise. |

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Quality assessment

Checks should be made on the analytical performance and where performance is found to deteriorate, an investigaiton should be made to identify where errors are occurring. During this check, no analysis of real samples should be made, and this analytical work should not be recommenced until the errors have been identified and corrected.

Often "odd" results can be spotted during the interpretation and evaluation of chemical data. It is important, therefore, to record and keep all details of analysis and calculation of results of analytical work so that a systemized check can be made to locate the source of the error. On some occasions, these errors can arise through mistakes in arithmetic work or transcriptional errors, eg. writing down a number incorrectly.

Data Storage Processing Reporting Dissemination

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It is important to record all analytical results and other relevant field data in a proper manner, ie. transfer data from rough laboratory and field books to the agreed record books once this data has been collected. This fair record should be maintained in a secure place. Whenever possible, results of investigations should be published in the open literature to ensure as wide a distribution of the results as possible.