REGIONAL SEAS

UNITED NATIONS ENVIRONMENT PROGRAMME OCTOBER 1990

Reference Methods and Materials

-a programmme of support for regional and global marine pollution assessments

Prepared in co-operation with

IAEA IOC

UNEP 1990

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Preface

This document describes a programme of comprehensive support for regional and global marine pollution assessments developed by the United Nations Environment Programme (UNEP) in cooperation with the International Atomic Energy Agency (IAEA) and the Intergovernmental Oceanographic Commission (IOC) and with the collaboration of a number of other United Nations Specialized agencies including the Food and Agriculture Organisation (FAO), the World Meteorological Organisation (WMO), the World Health Organisation (WHO) and the International Maritime Organisation (IMO).

Two of the principle components of this programme, Reference Methods and Reference Materials are given special attention in this document and a full Reference Method catalogue is included, giving details of over 80 methods currently available or in an advanced stage of preparation and testing. It is important that these methods are seen as a functional component of a much wider strategy necessary for assuring good quality and intercomparable data for regional and global pollution monitoring and the user is encouraged to read this document carefully before employing Reference Methods and Reference Materials in his/her laboratory.

Further general information on the activities of the three cooperating agencies in the marine pollution field may be obtained by consulting the UNEP (1985 brochure "Oceans and Coastal Areas" (new edition shortly available from OCA/PAC, see address on inside back cover); the IOC Technical Series document 25 (1984), "A framework for the implementation of the Comprehensive Plan for the Global Investigation of Pollution in the Marine Environment" (available from IOC at the address shown on the inside back cover) and the IAEA International Laboratory of Marine Radioactivity, Biennial Report 1987-1988 (available from MESL-ILMR at the address shown on the inside back cover). Any enquiries concerning details of the present document or the work of the agencies involved will also be welcome.

CONTENTS

1. Monitoring the Marine Environment - the need for comparable data.

Only three decades ago marine pollution was not an issue in the public eye. During the 1960's, however, there was a turning point when the effects of pollution became apparent and major catastrophic incidents were reported by the world's press - the Torrey Canyon sinking (off the coast of England) made the public intensely aware of oil pollution - the large scale and tragic poisoning by methyl mercury at Minamata, Japan, demonstrated the risks of heavy metals - and the evidence of bioaccumulation of DDTs and eggshell thinning by marine and terrestrial birds shortly after the publication of Rachel Carson's "Silent Spring" heightened public fears of chlorinated pesticides. Three decades ago, however, adequate analytical techniques were not widely available for chemists to quantify contaminants causing pollution and to assess their impact. With the increased concern for measuring potential pollutants in the marine environment, techniques were rapidly adapted from other areas of pure and applied chemistry and a large number of methodologies and data sets began to appear in the scientific literature.

Some of the data sets initially published were not consistent, particularly at the lower background or "baseline" concentrations. In some cases sporadic improvements in analytical strategies brought surprising changes in our knowledge of baseline concentrations - an apparent lowering in the baseline seawater concentrations of lead of 3 orders of magnitude in 4 decades, 3 orders of magnitude for tin in 2 decades and 1 order of magniture for mercury in 1 decade. Early international intercalibration exercises also revealed very large differences between analyses performed in different laboratories, particularly for organic parameters where coefficients of variation of over 50% were common. In order to evaluate spatial or temporal trends in contaminant concentrations, to define criteria (and in some cases legislation) for coastal water quality and to interpret biological effect studies, there was a clear need for intercomparable data of the best generally available precision.

Since the early days of marine pollution studies, the field has developed very rapidly. An intercalibration exercise on trace metals in tuna conducted in 1969 brought together only 17 scientists - a similar exercise in 1988 has involved more than 250 specialists (and these are probably only a small fraction of the total involved in this work). We are now aware of a vast number of contaminants in the marine environment and some (such as PCB's) are complex commercial formulations in which some components are highly toxic and others are not. New threats to the marine environment have been identified - some, such as the extremely toxic tributyl tin were probably barely present two decades ago and others such as plastic floating waste, human-induced eutrophication and the presence of pathenogenic bacteria and viruses may have been gradually worsening over a much longer period of time. More sophisticated techniques are now being developed and tested to quantify the biological effects of pollution at the sub-lethal level. The published scientific literature on marine pollution is abundant, and distributed over more than 30 journals, some of which are dedicated exclusively to this field.

For the more inexperienced scientists, keeping abreast of the scientific literature on methodology is a daunting challenge and it would be difficult to test the many hundreds of methodological modifications (not always improvements) published each year. Most conventional textbooks cannot be re-edited with sufficient rapidity to keep up with the pace of these developments. Clearly a more dynamic and flexible approach to this issue is required. The UNEP Reference Methods for Marine Pollution Studies series was established in 1983 as an attempt to address this issue and to provide a mechanism for testing, optimizing and updating methodologies and communicating them to marine scientists throughout the world.

The very best method is not always that which is chosen even by the more experienced scientists. Sometimes, very accurate and sensitive proceedures may require highly sophisticated instruments which are beyond the financial or technological capabilities of many environmental laboratories. In many cases the best available alternative techniques must be sought which utilize widely available and easily serviceable equipment but which give data of sufficient accuracy for meaningful monitoring of contaminants. A good method for measuring the contaminant is often not sufficient to conduct a meaningful pollution assessment. Guidelines for a satisfactory sampling strategy must be devised and the samples must be taken in such a way as to avoid contamination. Background chemical, physical and meteorological information may be required and the contaminant measurements themselves should be supported by well established quality assurance procedures. Finally, well-tested techniques should be available for evaluating the toxicity of the contaminant to selected organisms both at sub-lethal and acute (lethal) levels.

Having a good method alone does not necessarily ensure good data quality. In order for any method to generate comparable data it should be used with good quality assurance practices including employment of reference materials. Reference materials are large homogeneous batches of environmental samples for which a number of analytical parameters have been accurately determined and certified. The analyst periodically measures Reference Materials alongside his samples of unknown concentration and checks that the results he is obtaining for these materials are the right ones (details of how this is done will be described later).

In the coming years pressure on the resources of the marine environment will continue to increase as demands for food, energy, raw materials, transport and recreation grow and as mankind continues to use the oceans for intentional or accidental disposal of waste. The coastal zone is where this environmental stress will be particularly acute. By providing a flexible mechanism for technical support, adjusted to real environmental problems, the UN agencies are endeavouring to keep marine environmental scientists well-armed to face these challenges, not alone, but as part of a global team with a common aim.

2. A concerted action by the U.N. Agencies

Marine pollution does not usually respect the frontiers of coastal states and is often a regional, or even global, problem. Indeed, unless suitable criteria are agreed between neighbouring coastal nations, legal disputes may arise on such matters as recreational or shellfish-growing water quality, dumping, damage from accidental contaminant discharges, etc. Such matters are clearly within the competance of United Nations' Agencies and concerned regional organizations and for more than 25 years these have played an active role in international marine pollution affairs. The U.N. Conference on the Human Environment (Stockholm, 1972) developed a new "masterplan" for the protection of the world's environment which linked environmental assessment, environmental management and supporting measures for a global strategy. Since the Stockholm conference, the United Nations Environment Programme (UNEP) has served as a focal point for environmental actions and co-ordination within the U.N.-system. In 1974, the Regional Seas Programme of UNEP was initiated and a series of Regional Seas Action Plans were formulated to meet the specific needs of distinct geopolitical regions. Ten of these plans have now been adopted including over 120 coastal States.

The Intergovernmental Oceanographic Commission formulated its comprehensive plan for the Global Investigation of pollution in the Marine

Environment (GIPME) in 1976 and has established several regional contaminant monitoring networks, often in close cooperation with UNEP. It has also coordinated important studies of contaminants in the open ocean. Apart from UNEP and IOC, several other United Nations Agencies are closely collaborating in programmes concerning marine pollution: FAO (Food and Agriculture Organization), IMO (International Maritime Organization), WMO (World Meteorological Organization), WHO (World Health Organization), and IAEA (International Atomic Energy Agency).

One of the basic components of the action plans sponsored by UNEP (in the framework of its Regional Seas Programme) and of the regional subsidiary bodies of IOC, is the assessment of the state of marine pollution, of the sources and trends of the pollution and its effects on marine life. Unless the data gathered by regional and global monitoring programmes is comparable and of adequate quality, the assessments would be worthless. With this concern in mind, the UN Agencies are implementing a programme of technical assistance which includes the best expert advice, the most suitable reference methods and guidelines, adequate training and the provision of reference materials. Additionally, all international monitoring programmes require participation in a closely coordinated quality assurance programme which includes intercalibration exercises and regular data review.

Much of the technical support required for these activities has been provided from IAEA's International Laboratory for Marine Radioactivity (which is concerned with both nuclear and non-nuclear pollutants) and the IOC. Since 1974, the ILMR has acted as intercalibration centre for UNEP-sponsored marine programmes, and since 1984, has taken the responsibility of the technical aspects and the co-ordination of the development of the various Reference Methods. A major activity of IOC's GIPME is the coordination of three specialized groups of international experts: the Group of Experts on Methods Standards and Intercalibration (GEMSI, jointly sponsored by IOC and UNEP); the Group of Experts on the Effects of Pollutants (GEEP, jointly sponsored by IOC, UNEP and IMO); and the Group of Experts on Standards and Reference Materials (GESREM, jointly sponsored by IOC, IAEA and UNEP). These groups formulate and review relevant Reference Methods and, in the case of GESREM, cordinate the production and distribution of reference materials. The Groups provide the scientific and technical advice required for specific needs and ensure that the basis for the regional data retrieval programmes are scientifically sound. The Groups of Experts are also responsible for much of the research and development component required for keeping the programme up-to-date. Each of the Groups has 10 to 15 members, experts in their fields, participating in regular meetings and intersessional activities. The experts' participation in the work of the Groups is invited on a rotation basis so as to cover the range of expertise needed, and include appropriate geographical coverage.

By closely coordinating the work of UNEP, IAEA and IOC, together with specialized support from FAO, WHO, WMO and IMO, the present programme offers a comprehensive multidisciplinary package of technical support for the assessment of marine pollution using the most appropriate techniques and the best available expert advice.

The cooperating UN Agencies offer other forms of technical assistance to regional and global marine pollution monitoring programmes. This includes training courses, expert advice on methodology, assistance with emergency or pilot studies of marine pollutants, specialized workshops and instrument maintenance services. Further information on any of the support activities offered by UN agencies can be obtained by writing to one of the three addresses in the back cover of this document or to any of the other relevant specialized agencies belonging to the United Nations.

3. Reference Methods for Marine Pollution Studies

There are now over 70 Reference Methods published or shortly to be issued for testing and many are already available as French or Spanish translations. The methods are now being used by investigators in the UNEP and IOC sponsored marine research and monitoring programmes in order to ensure the global comparability and the necessary quality control of data. They are also extensively employed for training courses. In addition, some of the reference methods have been adopted by Governments as standards in discharging their obligations under regional agreements negotiated under UNEP's auspices. In parallel to the development of Reference Methods, regional and global intercalibration exercises are being conducted by IAEA (in collaboration with IOC and UNEP). These are showing a general improvement in data quality but demonstrate the urgent need for a more concerted effort in the field of data quality assurance (QA) in its broadest sense (including training, instrument calibration and maintenance, the preparation of working reference materials, joint monitoring exercises, quality control and data review).

The Reference Methods programme provides a wide-ranging series of methods and guidelines for marine pollution studies. Each method is self-contained and is written to follow, as closely as possible, the format and terminology recommended by ISO (the International Organization for Standards). They are designed to be applicable throughout the world and to produce data of sufficient accuracy, reliability and precision to allow meaningful interpretation for the purposes of regional marine pollution studies, as well as inter-regional comparisons (and so to contribute to UNEP's Global Environmental Monitoring System, GEMS). It is important to realize that they are dynamic in approach and are not simple "cook books". This can be best illustrated by describing how they are developed, tested and reviewed (see also fig. 1):

On the basis of scientific evidence, an expert group advises the specialized UN Agencies that a particular contaminant requires monitoring within an internationally sponsored programme and the decision is made to develop a reference method or a set of guidelines. Following consultations with the coordinator of the programme and the agency or expert group concerned, an individual expert is requested to prepare a first draft. This is then edited and distributed to selected experts for appraisal and testing. The draft is then re-edited and, in the case of straightforward chemical methods, is reviewed and approved by an expert group (usually GEMSI) and the agencies concerned and issued as a "first edition method". In the case of biological and some biochemical methods, the method is issued as a "draft edition" following expert review (as testing is a more complex process). The methods are then tested in four ways:

(i) By running intercalibration exercises on "blind" (unknown contaminant concentration) samples and certified reference materials. This is applicable to chemical methods only.

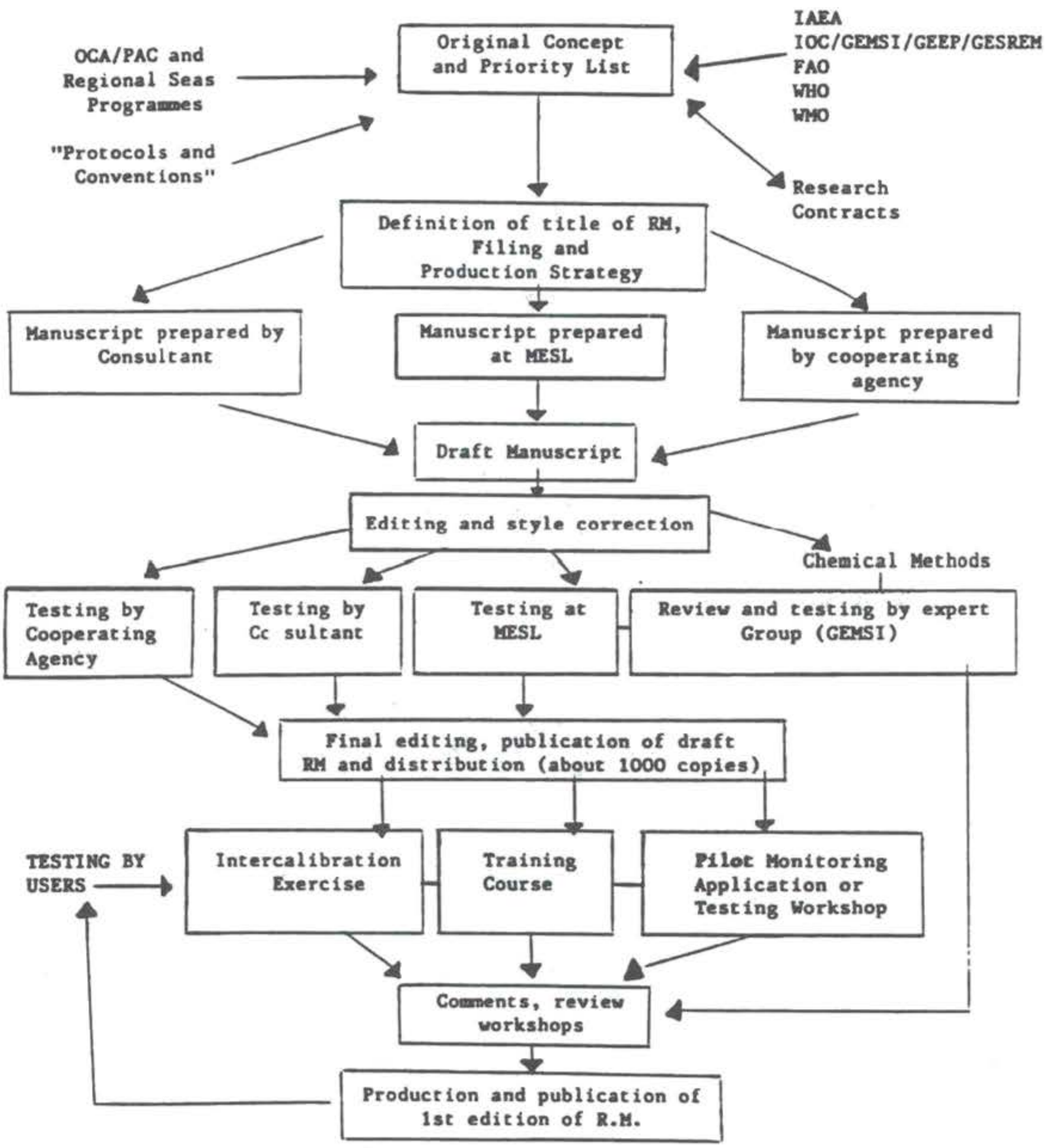
(ii) By international workshops, prior to which experienced scientists requested to test the methods alongside their own preferred methodologies.

(iii) By applying them in training courses.

(iv) By using them in Regional pilot monitoring exercises.

Results of these tests are periodically evaluated and whenever modification is found necessary, a new edition (Rev. 1,2,3, etc.) is issued. In the case of "draft" methods, satisfactory testing permits publication of the first definite edition. All users

Figure 1. Schematic representation of the steps in the production of a Reference Method



are encouraged to correspond with the programme coordinator if problems are encountered in application of the methods. Reference Methods which have been thoroughly tested and found to satisfy the legal requirements of the countries participating in the Regional Seas Programme are submitted to the governments (at intergovernmental meetings) for formal adoption as mandatory methods in the context of specific Regional Seas Action Plans and Conventions.

The Reference Method Catalogue (Annex 1) gives a full listing of methods now available and those which are currently being prepared or tested. Many of the methods are inter-related to form a structured series of texts (see diagrammes in Annex 1) on monitoring strategy, sampling technique, analysis, quality assurance and data interpretation. Each text is self-contained and can be updated without altering the rest of the series. The reader should make sure he has the latest edition of each method he or she requires. Many of the methods are now also available in French and Spanish indicated by "S" or "F" in the catalogue).

A brief description now follows of the fields covered by the Reference Methods:

3.1 The Sanitary quality of coastal waters

The public is becoming increasingly aware of sewage contamination of the coastal marine environment, particularly bathing beaches and adjacent waters. Holiday resorts, such as those of the northern Mediterranean, more than double in population during summer months and water quality in these areas may visibly deteriorate. Bacterial, viral and other pathogens often contaminate shellfish-growing waters to be concentrated in the shellfish with obvious human-health consequences. Measuring such dangerous pathogens as *Salmonella typhi* (which causes typhoid fever) and the hepatitis virus is no easy matter, however, and their presence is often only inferred from measurements of faecal coliform indicators. Indeed, although there is no demonstrable correlation between these indicators and pathogens (except for *Salmonella*), several countries have introduced norms of sanitary water quality based upon the faecal coliform index. For the Reference Methods, WHO has supplied a series of texts which explain in detail how to enumerate faecal coliforms and some pathogens (streptococci, *salmonella, Staphyloccus aureaus, Pseudomonas aeriginosa*) in seawater, sewage, sediments and bivalves. Before attempting to perform any of these tests the reader should consult Reference Method 1 (Rev. 1) which gives recently revised guidelines for monitoring the quality of coastal recreational and shellfish-growing waters and explains the limitations of the methods, advises on appropriate sampling strategies and reviews current developments in the field. A series of statistical methods for interpreting the results of the tests is provided as RM 55.

3.2 Chemical contaminants in marine ecosystems, sediments, the sea and the atmosphere

Sections 2 to 7 of the Reference Methods catalogue (Annex 1) describe the measurement of an extensive range of inorganic and organic chemical contaminants of the marine environment. The initial selection of these contaminants was not a casual one but corresponded to priorities ("blacklist contaminants") set by various conventions (such as the London Dumping Convention; the

Barcelona Convention for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources; etc.). The catalogue also includes guidelines for measuring some contaminants not cited in these conventions but which may become a problem in the next decade and should be subject to exploratory monitoring.

Section 2 specifies methods for measuring chemical contaminants in marine organisms. RM No. 6 describes the use of sentinel organisms for monitoring marine contaminants and methods 7 and 12 show how to sample the selected organisms for trace metals and organic contaminants respectively. Analytical techniques are described for trace metals (cadmium, zinc, lead, copper, mercury, selenium and arsenic), chlorinated hydrocarbons (DDTs and PCBs) and methyl-mercury. The list will shortly include a new simplified and improved procedure for methyl mercury, a procedure for organotin and guidelines for the determination of organophosphorus compounds. Method 14 shows how to measure DDTs and PCBs by packed column gas chromatography. Through this method is a useful screening procedure, much better resolution and more accurate results can be achieved with capillary gas chromatography and full details of this procedure are given in the recently published method 40.

Section 3 addresses chemical contaminants in sea water. Routine measurements of dissolved contaminants are not normally made in regional monitoring programmes - it is very difficult to assure data quality and intercomparability. The two current exceptions are petroleum hydrocarbons and organotins which are important basic methods for routine monitoring studies.

By measuring contaminant concentrations in sediments, important information can be obtained on contaminant gradients, historical changes (from dated core samples) and sources and fates of the contaminants themselves. Experimental (or monitoring) strategy, sampling techniques and data interpretation are somewhat more complex than with sentinel organisms however. For example, trace metal contamination must be discerned from natural background levels which in turn vary with the geochemistry of the sediments themselves (e.g., particle size, mineralogy, organic matter content, redox environment, provenance). Appropriate strategies are presented in RM 58 (Guidelines for the use of sediments for marine pollution monitoring programmes). Section 4 of the catalogue (Annex 1) also lists methodologies for an extensive series of variables which can be determined in marine and estuarine sediments. These include trace metals, petroleum hydrocarbons and chlorinated hydrocarbons.

The particular problems of monitoring estuaries are considered in a special series of Reference Methods (Section 5 of the catalogue). The series includes guidelines for collecting and interpreting data from estuaries (RM "C"), guidelines for the determination of riverine inputs of contaminants to estuaries (RM 41) and specific techniques for measuring mercury, cadmium, total phosphorus, total nitrogen and biochemical and chemical oxygen demand. By employing the two sets of guidelines, the user should be able to conduct meaningful studies of estuaries and evaluate rates of inputs of contaminants to the system and through the system to the sea.

Floating and beached debris is another matter of global and regional concern. Tar balls (largely produced by the accidental or intentional discharge of oil to the sea) are to be found on all of the world's beaches, sometimes in huge quantities which spoil their amenity value and damage inter-tidal ecosystems. Measurement of tar ball density can be done with virtually no equipment but produces a scientifically valuable measure of oil pollution (see Ref. Meth. 15). Floating debris often also includes plastic waste (and garbage), ranging from tiny beads of polystyrene used as packing material, to large polyvinyl sheets and discarded nylon fishing nets (see Ref. Meth. "X").

A series of methods have been designed to measure atmospheric chemical contaminants in the marine and coastal environment. Method 24 shows how to sample aerosols and wet precipitation for chemical analyses and Ref. Meth. 42 gives guidelines for the determination of selected trace metals in the samples thus obtained. Methods are also planned for sampling dry deposition (a particularly difficult procedure to perform quantatively) and for the determination of halogenated hydrocarbons in wet precipitation and aerosols.

Some other miscellaneous Reference Methods complete the spectrum of techniques for chemical contaminants. Method "AD" will give guidelines for measuring used lubricating oils in the marine environment (often a series problem in the coastal marine environment near large cities and industrial centres) and method "AF" will show how to clean-up reagents and glassware for low-level contaminant monitoring. Method "AF" will be essential information for anyone interested in open-ocean measurements, particularly of organic parameters, in countries where ultra-pure reagents are not readily available.

3.3 Biological effects of marine contaminants

It is vitally important for environmental scientists to be able to quantify the biological effects of the contaminants they are measuring in order to develop criteria for improved environmental management. With its new emphasis on biological effects measurements at the acute, sub-lethal and community levels, the Reference Methods series hopes to contribute to resolving some of the major methodological difficulties in this field.

Three types of methodology for assessment of biological effects are contemplated in the "Reference Methods" series: Acute toxicity tests (lethal levels); Tests of sub-lethal effects; and contamination induced alterations in marine ecosystems. Reference Methods 43, 44 and 45 provide a series of relatively simple acute toxicity tests. These tests were evaluated in an inter-laboratory trial of Mediterranean laboratories before being published as first definite editions in 1989. The Spanish language versions have also been put to immediate use in a regional training workshop in 1988 in Cartagena, Colombia.

The production of reliable toxicity tests for sub-lethal effects is a much more complex issue. This task has been a major item on the recent agenda of the IOC/UNEP/IMO Group of Experts on the Effects of Pollution (GEEP) and suitable techniques have recently been tested by them in workshops in Oslo and Bermuda. The first biochemical techniques developed by the group (Ref. Meth. "J") will become available as Reference Methods in early 1991 and will represent an important innovation in methodology for marine pollution studies.

Various aspects of marine ecosystem alteration are considered in the Reference Methods programme. Guidelines for monitoring coral reefs and for sampling and identifying jellyfish (blooms have sometimes been associated with eutrophication) are available as Ref. Meths. 25 and 5l. GEEP is preparing a set of guidelines for evaluating the effects of thermal discharges on the marine environment. The development of a set of guidelines for detecting and monitoring eutrophication in the marine environment is also planned (Ref. Meth. "AH").

3.4 Background data for studying contamination

In order to be able to interpret contaminant measurements, additional background information should also be obtained. Section 9 of the catalogue presents three useful sets of guidelines and techniques for the obtention of physical, meteorological and chemical oceanographic data respectively. These Reference Methods contain information on how to measure currents, temperature and salinity distributions, depth, wind, rainfall, sea conditions, dissolved oxygen, pH, nutrients, hydrogen sulphide, etc., etc. They are also useful for more general studies and training purposes and have passed the same rigorous review procedures as the more specific methods for chemical contaminants.

4. Guidelines and Reference Materials for data quality assurance

Even when supplied with an unambiguous and well-tested Reference Method, the (careless?) analyst can easily make serious errors which invalidate his data. For this reason it is important that staff are properly trained and a well-conceived quality assurance (QA) strategy is adopted in all analytical laboratories performing environmental measurements. Staff should be trained in chemistry and in handling the glassware, reagents and equipment required for each method. Also, the analyst should know how to calibrate and optimise his instruments and fully understand how they operate (in order to be able to distinguish between his own operational errors and technical faults in the equipment). Cleanliness is vital for making low-level measurements of contaminants. The analyst should always be wary of possible sources of contamination - dust, "bad" distilled water, dirty reagents or glassware. This "analyst's sixth sense" cannot be written into a reference method.

Fortunately there are techniques for maintaining data quality at its best. The analyst can check his results by analyzing a Certified Reference Material (CRM) of a matrix similar to his own samples but containing a known concentration of a number of analytes. All laboratories monitoring contaminants should also participate in the intercalibration exercises organised by IAEA or ICES (participation is obligatory for laboratories submitting data to some Regional Action plan data banks). Some of these

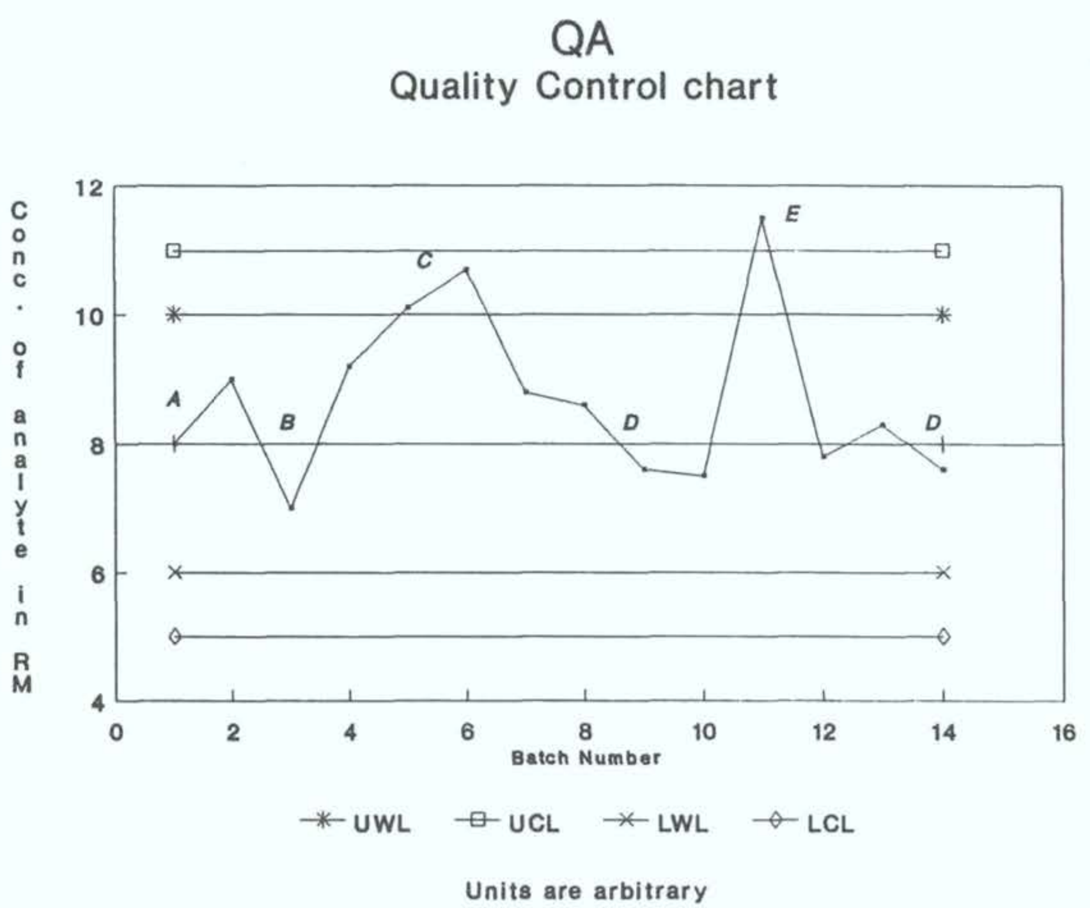


Figure 2. An example of a Quality Control Chart.

ANNOTATIONS

A - A "consensus value" is established by repeated analyses of a RM. Upper and lower warning and control limits are determined statistically from the standard deviation (s) of the n measurements made.

B - The routine measurements of the RM are well within the warning limits. Measurements are under control.

C - Something appears to be contaminating the samples here. Reagents were investigated and a new batch of solvents was found to be at blame and was replaced immediately.

D - The process is back under control.

E - Here, a serious problem was discovered. The previous ten data were rejected and all analyses were discontinued until the fault (dirty glassware this time) was detected and corrected.

exercises include more than one hundred participants and the data is sufficiently well statistically grouped ("consensus" values) to "certify" the intercalibration material for future distribution as a CRM.

Careful evaluation of the results of intercalibration exercises tell us how well a particular analyte can be determined and which laboratories are not performing correctly. They provide a means for analysts to compare their data quality (confidentiality is maintained and each lab is assigned its own "secret code number"). They do not, however, provide analysts or lab managers with day-to-day feedback on their precision and accuracy. This requires a Quality Control (QC) process. The principle is quite simple. Staff of monitoring laboratory obtain or prepare a large batch of a sample with a similar matrix to that which they are usually measuring. The sample is homogenized and dried (or better, lyophilized) and analyzed on a number of occasions alongside CRMs. Once an acceptable analytical mean and coefficient of variation are found, the sample is declared an Internal Reference Material (IRM). The IRM is then included as an additional sample to be measured, after about every 10 monitoring samples determined by the monitoring lab. (i.e., 10% of all laboratory effort should be dedicated to QC). The results for the IRM measurements are plotted on a "Quality Control" chart (see example in Fig. 2). When the IRM value falls outside defined control limits the results from the previous 10 analyses are discarded and sample analysis is resumed only when new measurements of the IRM give satisfactory results again. A combination of good laboratory practice and quality control based on CRMs, intercalibration exercises, IRMs and QC charts should guarantee data of the highest possible quality.

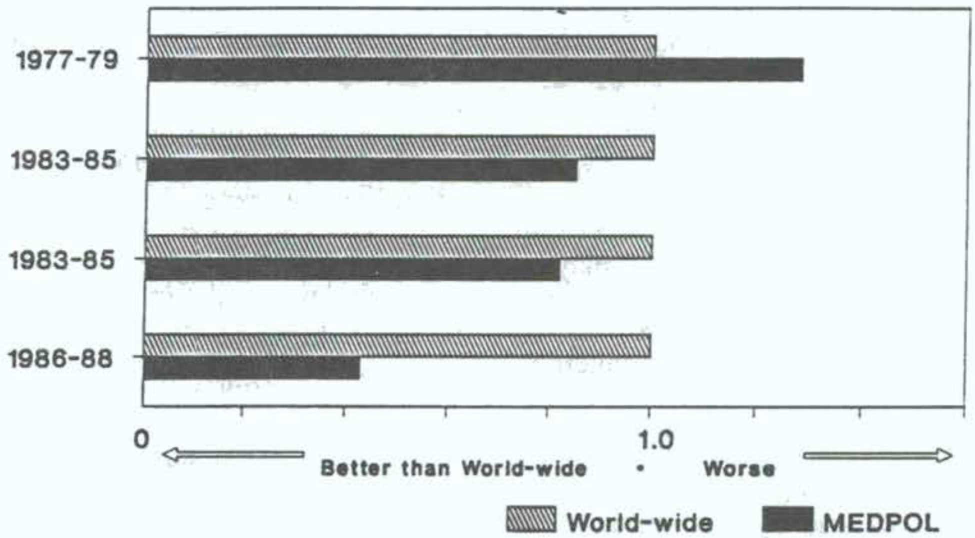
Of course, in order to apply these principles, full details of the procedure are necessary. These are included in a set of "Reference Guidelines on Quality Assurance Procedures". It should be remembered that Quality Assurance implies making sure that the data is good enough for an intended purpose. Data of sufficient precision for detecting contaminant hot spots may not be good enough for measuring long-term trends in the open-ocean (but also requires much less analytical effort). Quality assurance procedures cover all aspects of contaminant measurement including monitoring strategy and data management.

An expert group, GESREM (see section 2), coordinates the international efforts to produce CRMs for marine matrices. The present cost of the packaged material to the public rarely reflects the high production (and calibration) costs of these materials and by combining the efforts of various producers, GESREM will assure future supplies of suitable materials. Standards, such as pesticide mixtures and CRMs are listed in a catalogue produced by NOAA (USA) in coordination with GESREM (and available cost free from IOC at the address given in the inside back cover). The best way to obtain CRMs (free of charge) is to participate in an intercalibration exercise. When you receive the final report of the exercise (only sent to participants submitting data) it includes provisional consensus certification values for a large range of analytes for the material you have left over (you normally only use about 10% of the original material for the purpose of the exercise itself). For certification, consensus must be achieved for results from more than one independant analytical method.

5. Looking towards the future

Is all this extra effort worthwhile? Close attention to data quality has already brought some promising improvements. Figure 3 illustrates this point for trace metal data in the MEDPOL Programme. Results are shown for statistically pooled coefficients of variation (a measure of precision) for four intercalibration exercises on homogenized, lyophilised, biota distributed both worldwide and to MEDPOL laboratories The first exercise (before the MEDPOL Programme began) showed that Mediterranean laboratories lagged behind the world average. As the MEDPOL programme advanced, the data quality improved considerably. With good quality data, the Mediterranean monitoring programme now makes a meaningful contribution to the environmental protection and development of the region. Unfortunately, for some variables, (particularly organic chemical pollutants) neither global nor regional indices of data are adequate as yet and considerable attention to methods, standards and data quality assurance are still required in order to achieve sustainable improvements. This work will require an even greater effort in the next decade as more and more organic chemical contaminants and their degradation products are discovered.

Figure 3. Trace Metal Data Quality (Marine Biota) MEDPOL and Global Intercalibration



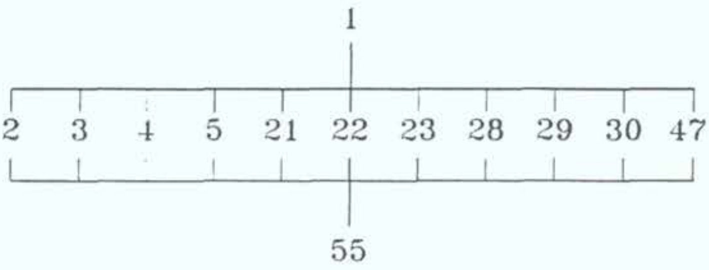
Pooled coefficient of variation (for Cd, Cu, Hg, Mn, Pb). Normalised to 1 for the world-wide exercise.

Annex 1. A CATALOGUE OF REFERENCE METHODS

This catalogue shows the Reference Methods currently available, those in revision (shown by numbers and "in preparation") and those planned for 1991-92 (shown by letters and "in preparation"). Translations are indicated by letters (E-English, F-French, S-Spanish). The methods are available free of charge from OCA/PAC or MESL at the addresses shown on the inside, back cover.

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

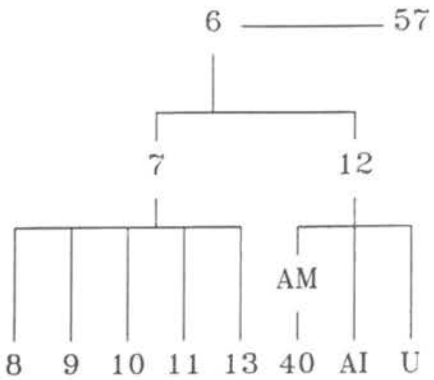
No. 1	UNEP/WHO: Guidelines for monitoring the quality of coastal recreational and shellfish-growing waters.	Rev.1(E) 1988 Rev.1(F) 1988 Rev.1(S) 1991
No. 2	UNEP/WHO: Determination of total coliforms in sea water by the membrane filtration culture method.	Rev.1(E) 1983 Rev.1(F) 1983
No. 3	UNEP/WHO: Determination of faecal coliforms in sea water by the membrane filtration culture method.	Rev.1(E,F) 1983
No. 4	UNEP/WHO: Determination of faecal strepto-cocci in sea water by the membrane filtration culture method	Rev.1(E,F) 1983
No. 5	UNEP/WHO: Determination of faecal coliforms in bivalves by multiple test tube method.	Rev.1(E,F) 1983
No. 21	UNEP/WHO/IAEA: Determination of total coliforms in sea water by multiple test tube (MPN) method.	draft(E) 1985 draft(F) 1987
No. 22	UNEP/WHO/IAEA: Determination of faecal coliforms in sea water by multiple test tube (MPN) method.	draft(E) 1985 draft(F) 1987
No. 23	UNEP/WHO/IAEA: Determination of faecal streptococci in sea water by multiple test tube (MPN) method.	draft(E) 1985 draft(F) 1987
No. 28	UNEP/WHO/IAEA: Determination of staphy-lococcus aureus in sea water and sewage by the membrane filtration culture method.	draft(E) 1986
No. 29	UNEP/WHO/IAEA: Determination of pseudomonas aeruginosa in sea-water and sewage by the membrane filtration culture method.	draft(E) 1986
No. 30	UNEP/WHO/IAEA: Isolation/enumeration of salmonella from sea water and sewage.	draft(E) 1986
No. 47	UNEP/WHO/IAEA: Determination of faecal coliforms in estuarine waters, suspended matter and sediments.	draft(E) 1991 draft(F) 1990
No. 55	UNEP/WHO/IAEA: Statistical methods for the evaluation of results from monitoring the quality of coastal recreational and shellfish -growing waters.	draft(E) 1989 draft(F) 1989
"AC"	UNEP/WHO/IAEA: Determination of selected neurotoxins in marine organisms.	in preparation



2. Chemical contaminants in marine organisms

No. 6	UNEP/FAO/IOC/IAEA: Guidelines for monitoring chemical contaminants in marine organisms.	draft(E) 1990
No. 7	UNEP/FAO/IOC/IAEA: Sampling of selected marine organisms and sample preparation for trace metal analysis.	Rev.2(E) 1984 Rev.2(S) 1988
No. 8	UNEP/FAO/IOC/IAEA: Determination of total mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry.	Rev.1(E) 1984 Rev.1(S) 1987
No. 9	UNEP/FAO/IAEA: Determination of total arsenic in selected marine organisms by hydride generation atomic absorption spectrophotometry.	draft(E) 1985
No. 10	UNEP/FAO/IAEA: Determination of total selenium in selected marine organisms by hydride generation atomic absorption spectrophotometry.	(E) 1984
No. 11	UNEP/FAO/IOC/IAEA/: Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry.	Rev.1(E) 1984 Rev.1(S) 1984
No. 12	UNEP/FAO/IAEA: Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons.	Rev.1(E) 1984 Rev.1(S) 1987
No. 13	UNEP/FAO/IAEA: Determination of methylmercury in selected marine organisms by gas chromatography.	(E) 1984 (S) 1988 Rev.1 (in prep)
No. 14	UNEP/FAO/IOC/IAEA: Determination of DDTs and PCBs in selected marine organisms by packed column gas chromatography.	Rev.1 (E) 1986 Rev.1 (S) 1988
"AM"	UNEP/IOC/IAEA: Determination of chlorinated hydrocarbons in marine organisms: Sample extraction and clean-up.	in preparation
No. 40	UNEP/IOC/IAEA: Determination of DDTs and PCBs in selected marine organisms by capillary column gas chromatography.	(E) 1988
"AI"	UNEP/IOC/IAEA/FAO: Determination of petroleum hydrocarbons in selected marine organisms.	in preparation

"U"	UNEP/IAEA/IOC/FAO: Determination of organotin compounds and total tin in selected marine organisms.	in preparation



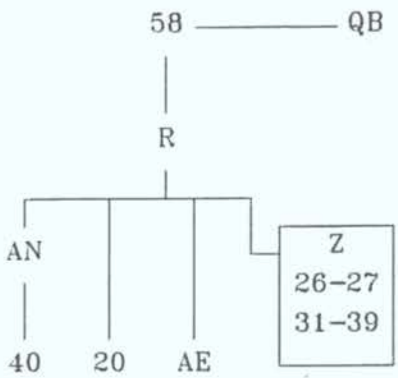
3. Chemical contaminants in sea water

No. 56	UNEP/IOC/IAEA: Determination of dissolved/dispersed hydrocarbons in marine waters.	(E) 1990
No. 59	UNEP/IAEA/IOC: Determination of butyltin compounds in coastal waters.	(E) 1990

4. Chemical contaminants in marine sediments and suspended matter

No. 58	Guidelines for the use of sediments for marine pollution monitoring programmes.	(E) 1990
"R"	Guidelines on the sampling and preparation of sediments for marine pollution monitoring.	in preparation
"AN"	UNEP/IOC/IAEA: Determination of chlorinated hydrocarbons in marine sediments: Sample extraction and clean-up.	in preparation
No. 20	UNEP/IOC/IAEA: The determination of petroleum hydrocarbons in sediments.	(E) 1990 (S) 1991
"AE"	UNEP/IOC/IAEA: Determination of organophosphorus compounds in marine sediments.	in preparation
No. 26	UNEP/IAEA: Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry.	draft(E) 1985
No. 27	UNEP/IAEA: Determination of total cadmium in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985
No. 31	UNEP/IAEA: Determination of total chromium in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985
No. 32	UNEP/IAEA: Determination of total cobalt in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985

No. 33	UNEP/IAEA: Determination of total copper in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985
No. 34	UNEP/IAEA: Determination of total lead in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985
No. 35	UNEP/IAEA: Determination of total nickel in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985
No. 36	UNEP/IAEA: Determination of total vanadium in marine sediments by flameless atomic absorption spectrophotometry.	(E) 1985
No. 37	UNEP/IAEA: Determination of total iron in marine sediments by flame atomic absorption spectrophotometry.	(E) 1985
No. 38	UNEP/IAEA: Determination of total manganese in marine sediments by flame atomic absorption spectrophotometry.	(E) 1986
No. 39	UNEP/IAEA: Determination of total zinc in marine sediments by flame atomic absorption spectrophotometry.	(E) 1986
"Z"	UNEP/IOC/IAEA: Determination of aluminium in sediments.	in preparation



5. Chemical contaminants in estuarine waters and suspended matter

"C"	UNEP/IOC/IAEA: Guidelines for collecting and interpreting data on estuaries.	(E) 1990
No. 41	UNEP/IOC/IAEA: Guidelines for the determination of riverine inputs of contaminants to estuaries.	(E) 1987
No. 19	UNEP/IOC/IAEA: Determination of total mercury in estuarine waters and suspended sediment by cold vapour atomic absorption spectrophotometry.	draft(E) 1985

No. 52	UNEP/WHO/IOC/IAEA: Determination of phosphorus in suspended matter and sediments.	in preparation
No. 53	UNEP/WHO/IAEA: Determination of nitrogen in suspended matter and sediments.	in preparation
G	UNEP/WHO/IOC/IAEA: Determination of BOD_5 and COD in estuarine waters.	in preparation
I	UNEP/IOC/IAEA: Determination of total cadmium in estuarine waters and suspended matter.	in preparation

6. Chemical contaminants floating or on beaches

No. 15	UNEP/IOC/IAEA: Monitoring of tar on marine beaches.	(E) 1985
"X"	UNEP/IOC/IAEA: Guidelines for quantifying persistant synthetic materials which may float, sink or remain in suspension.	in preparation

7. Atmospheric chemical contaminants

No. 24	UNEP/WMO/IAEA: Sampling of aerosols and wet precipitation for analysis of chemical pollutants.	draft(E) 1985
No. 42	UNEP/IAEA/WMO: Guidelines for the determination of selected trace metals in aerosols and in wet precipitation.	draft(E) 1988
P	UNEP/IOC/IAEA: Determination of halogenated hydrocarbons in aerosols and in wet precipitation.	in preparation
Q	UNEP/WMO/IOC/IAEA: Sampling of dry deposition.	in preparation

8. Effects on marine organisms and ecosystems

No. 25	SPC/UNEP: Coral reef monitoring handbook.	(E) 1984 (F) 1990
No. 51	UNEP: Sampling and identification of common Mediterranean Scyphomedusae and evaluation of their occurrence.	draft(E) 1988
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No. 45	UNEP/FAO/IAEA: Comparative toxicity test of water-accommodated fractions of oils and oil dispersants to marine organisms.	(E) 1989 draft(S) 1988

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9. Standard physical, chemical and meteorological observations

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10. Quality assurance procedures

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"QB"	UNEP/IOC/IAEA: Quality Assurance and Good Laboratory Practice for the measurement of contaminants in marine sediments	in preparation

11. Miscellaneous methods

No. 0	UNEP/IAEA: Guidelines for the use of Reference Methods in marine pollution studies.	(E).1990.
"AD"	UNEP/IOC/IAEA: Guidelines for monitoring the presence of used lubricating oils in the marine environment.	in preparation
"AK"	UNEP/IOC/IMO/IAEA: Guideline for monitoring marine dumpsites.	in preparation
"AL"	UNEP/IOC/FAO/WHO/IAEA: Guidelines for assessing the impact of point sources.	in preparation
"AF"	UNEP/IOC/IAEA: Reagent and laboratory ware clean-up procedures for low-level contaminant monitoring.	in preparation
No. 46	UNEP/WHO/IAEA: Determination of methyl-mercury, total mercury and selenium in human hair.	draft(E) 1987

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