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ENVIRONMENT AGENCY

REPORT ON THE
NATIONAL MARINE ANALYTICAL
QUALITY CONTROL SCHEME 1992/93
(MPMMG 93/12)

August 1993
Jessep/MAJ1/DH

NATIONAL MARINE ANALYTICAL QUALITY CONTROL SCHEME
FIRST INTERIM REPORT

EXECUTIVE SUMMARY

A National Marine AQC scheme has been established by NCC, as required by MPMMG.

It is designed to span as many of the NMP determinands as possible and, in fact, encompasses some 80% of the determinands listed in the NMP, the exceptions being some field determinands. For year 2 the scheme has been extended in line with proposed revisions to NMP.

The scheme has 21 participating laboratories, comprising most of the bodies represented at MPMMG. Membership and funding have been secured to operate the scheme for a second year.

A contractor to operate the scheme in year 1 was selected by open competitive tendering. The scheme has operated to schedule and to budget with quarterly distributions of test samples. A contract has been established for the second year of operation.

Results of the distributions to date indicate that overall performance was good in relation to that achieved in similar exercises for inter-laboratory water analysis especially if the low concentrations of interest are considered. There was an overall similarity in performance between RPB, NRA and Government laboratories.

The required standard of accuracy for nutrient determinations was met by a large proportion of participants. However, improved accuracy appears to be required in many instances for trace metals in water and in some laboratories for organic determinands.

Comparability for sediment and biota analysis was not adequate for metals or organic determinands.

Overall indications are that both analytical method and quality systems are important in achieving consistently good results. In fact, the laboratories with the highest level of participation and achievement of accuracy are those with formalised quality systems subject to scrutiny by external assessors.

A formal in-house AQC policy has been developed.

In the second year of operation, emphasis has been placed on targeting the identified problem areas and in developing laboratory quality systems. To this end the number of routine distributions has been reduced to two for the second year of the scheme, and resources diverted to special exercises for problem areas and the establishment of workshops.

A review is being undertaken of the quality aspects of sampling and sample handling.

Links have been established with the BCR QUASIMEME scheme.

APPENDICES

Appendices - continued

GLOSSARY OF TERMS

AQC	Analytical Quality Control
ICES	International Council for the Exploration of the Seas
MPMMG	Marine Pollution Monitoring Management Group
BCR	Bureau of Community Reference
DoE	Department of the Environment
FRPB	Forth River Purification Board
NRA	National Rivers Authority
MAFF	Ministry of Agriculture, Fisheries and Food
NCC	National Co-ordinating Committee
RPB	(Scottish) River Purification Board
SOAFD	Scottish Office Agriculture and Fisheries Department
DANI	Department of Agriculture Northern Ireland
PML	Plymouth Marine Laboratory
IOSDL	Institute of Oceanographic Sciences Deacon Laboratory
DOENI	Department of Environment Northern Ireland.
IRTU	Industrial Research and Technology Unit
Paris Commission (PARCOM)	The body who implement the Convention for the Prevention of Marine Pollution from Land based sources.
Annex 1A	Annex 1A of the Ministerial Declaration of the Third International Conference on the Pollution of the North Sea, The Hague, 8 March 1990.
NAMAS	National Measurement Accreditation Service
GCSDM	Group Co-ordinating Sea Disposal Monitoring.
NSTF	North Sea Task Force.
NMP	National Monitoring Plan
QUASIMEME	Quality Assurance of Marine Environmental Monitoring in Europe

GLOSSARY - Continued

TON   Total Oxidized Nitrogen.

LOD   Limit of Detection.

WRc   Water Research Centre.

JMG   Joint Monitoring Group of the Oslo and Paris Commissions.

1. INTRODUCTION

The requirements for and the establishment of the National Marine AQC scheme have been discussed in detail in the Interim Report (March 1993), reference 5, which was presented to the April 1993 meeting of the MPMMG.

## 2.	REPORT OF THE NATIONAL CO-ORDINATING COMMITTEE

### 2.1	Functions and Role of NCC and FRPB

2.1.1	At the first meeting of NCC on 18 February 1992, the requirement for a chairman and secretary was agreed and Dr M A Jessep (NRA Anglian Region) and Dr M Roberts (DoE) elected to these posts. It was agreed by those present (see Appendix 2.1.1) at the sixth meeting of the NCC on 7 May 1993 that Dr M A Jessep and Dr M Roberts should continue in post for a further year.

2.1.2	The roles of the NCC and FRPB (Appendices 2.1.2, 2.1.3) were formally agreed and a "prioritisation" of NCC responsibilities made at the first meeting on 18 February 1992.

### 2.2	Scope, Strategy and Development of the Scheme

2.2.1	With regard to NCC developing and managing a scheme to cover Biology and Microbiology, it was felt that it lacked sufficient in-depth knowledge of these fields to be able to establish and maintain such a scheme. It was felt that for the current NCC to take on this additional work would dilute the effort required to make progress with the chemistry scheme, and that to extend membership of NCC to introduce the necessary expertise would make the group unwieldy.

This view was endorsed at the MPMMG meeting in Bristol on 22 April 1993. NCC will therefore continue to concentrate on chemistry and target determinands listed in NMP. (Appendix 2.2.1).

Dr M Service (DANI) was requested by MPMMG to examine the feasibility of operating a Biological AQC Scheme.

2.2.2   The NCC has recognised the need to establish links with and stimulate collaboration with international inter-comparison exercises. Dr D Wells (SOAFD) has therefore been tasked with presenting to NCC status reports regarding the BCR initiative - QUASIMEME.

Several of the laboratories participating in the UK national scheme participate in the QUASIMEME scheme (see Appendix 2.2.2). This should ensure cross fertilisation of ideas, facilitate solutions to problems and help in the development of standard reference materials where required.

Recently, an ad hoc group of NCC explored further with WRc the potential for links between the National Scheme and QUASIMEME. It concluded that from 1994 onwards there were benefits to both schemes by establishing informal links with regard to availability of sediment and biota materials developed for use in QUASIMEME, both for use within the scheme and as working reference materials.

2.2.3   Information gathering on the status of in-house AQC schemes was delayed until the external scheme had been established; in late 1992 a questionnaire was circulated.

The Chairman with assistance of Mr M G Firth (NRA Yorkshire Region) produced a discussion document for the 6th meeting of NCC in May 1993. Following amendments this document will be presented to the 7th meeting in September 1993 for all participants to adopt as policy.

2.2.4   An overview of how the scheme is intended to operate is shown in Appendix 2.2.4. "In-house" AQC should provide a "continuance of cover". Adoption of similar approaches to in-house AQC by participating laboratories (see Section 2.2.3) should enable the information gathered to be reviewed more easily and provide a useful basis for a more sound

interpretation of the problems encountered both in the National and International AQC schemes.

2.2.5   The National Marine AQC scheme has provided useful information in its first year of operation. It was concluded by NCC that a similar scheme should be continued for a second year in order to provide data on the performance of laboratories and to give users of NMP data a clear indication of its quality. Options for the second year were discussed at the 6th meeting of NCC on May 1993, when it was agreed that (1) the scheme would be extended to cover determinands listed in NMP, (2) biota would be included in every exercise in order to obtain more rapidly an assessment of the quality of this data, (3) the exercises would be reduced in frequency to twice per annum. In addition, special exercises would be undertaken, targeting areas of concern or poor performance (Appendix 2.2.5).

2.2.6   The establishment of ad hoc groups to examine in detail particular intransigent problems was delayed until the results of initial exercises could be assessed. At the 6th meeting of NCC the need for such groups was identified and two areas of concern targeted (a) mercury analysis at low levels and (b) organics analysis in the water column. Proposals were accepted for the establishment of two workshops - plans are under way with regard to running a workshop on mercury analysis in Autumn 1993. The organics workshop is likely to follow in early 1994.

2.2.7   NCC has provided useful support to participants by dissemination of information. A list of documents circulated is shown in Appendix 2.2.7.

2.2.8   The NAMAS accreditation scheme, run by the National Physical Laboratory (NPL) was thought to have an essential part in ensuring long term quality assurance within UK laboratories. The scheme is also recognised within the EEC and is equivalent to EN 45000.

In view of the workload involved in achieving accreditation, no timetable was set by NCC. However, some progress has been made; a current status report is included as Appendix 2.2.8.

It should be noted that not all laboratories listed as having achieved · NAMAS accreditation are currently accredited for the determinands of interest at a level thought relevant to NMP purposes.

2.2.9 Sampling and sample handling have long been recognised as major sources of concern in achieving good quality chemical information; the lower the range of interest the more marked are the concerns in these areas.

Although the NCC had recognised these problems, it was considered at early meetings that their resolution would require considerable effort and that the input of this effort should be delayed until the external scheme was operational.

Mr R .Law (MAFF) has now been requested to collate available information on sampling and sample handling and to make this information available to NCC. Papers have been circulated to all participating laboratories (see Appendix 2.2.7). It is the intention of NCC that a set of documents will eventually be produced, and to this end Mr R Law (MAFF) and Dr D Wells (SOAFD) have been requested to produce discussion papers on aqueous samples and sediment/ biota respectively.

2.2.10 Following discussions with Dr Davies (SOAFD), NCC agreed that rather than adopt a recipe book approach to methods of analysis, it would:

- List the range of detection required for each determinand/ matrix in each area.
- Recommend suitable methods for each determinand.
- Recommend AQC procedures for each determinand.

However, to provide an accurate picture would require examination of the information on methods gathered from questionnaire returns together with results from several exercises, and it was therefore agreed that in the interim NCC would produce data for LODs for each determinand/matrix and a provisional list of methods. This is discussed further in Section 4 of this report and in the "Interim Report on Marine Methods produced by Dr A Griffiths (FRPB) (reference 4).

NOTE:

Although in general, the NCC concluded that laboratories should not be constrained to a particular method, exceptions to this rule were accepted for those determinands/determinand groups where the result would be dependent on the manner in which the sample was prepared eg particle size fraction, method of digestion of sediments for metals analysis.

Sediment digestion techniques for metals analysis were discussed by NCC and it was agreed that all laboratories would adopt a common approach.

For <u>AOC scheme purposes</u> aqua regia was agreed as an interim technique. This decision was taken since few of the participating laboratories were using hydrofluoric acid (HF), it was desirable to remove a source of variation from the exercises, and that aqua regia would continue in use for samples taken for non-NMP purposes.

Discussions at MPMMG in April 1993 regarding the use of HF has led to clarification in a recent communication by Dr J Portmann (MAFF) to the chairman NCC in which HF digestion is interpreted as a requirement for NMP to give "total" metal data.

2.2.11   Concern has been expressed by WRc and within discussions at the NCC on two counts;

(i) there was currently no way of auditing NMP data to ensure that the laboratory providing the information had participated in the AQC schemes.

(ii) some laboratories were not participating on a continuous basis ie having failed in previous exercises were no longer providing data.

At the MPMMG meeting in April 1993 it was agreed that all "bodies" providing NMP data would be sent a questionnaire to confirm their intended data provision; this has been done and their responses are being collated. It was also agreed that all NMP data not subject to the National Marine AQC scheme would be "flagged".

2.2.12 In due course it may be necessary to provide for a second "flag" to indicate where the data has been subject to the AQC scheme, but the performance of the laboratory failed to meet specified standards.

2.3 **Development of the Tender**

2.3.1 The development of the initial tender has been discussed in detail in the Interim Report on the National Marine Analytical Quality Control Scheme 1992/3 (Reference 5).

2.3.2 The development of the tender for the second year of the scheme has been referred to earlier in this section. Given limited resource NCC felt that to achieve its twin aims of continuity and improvement the approach to the second year of the scheme would be to reduce the frequency of routine exercises and divert resources to particular problem areas. (See Appendix 2.2.5).

2.3.3 The "Level of Interest" (See Appendix 2.3.3(1)(2)(3)) for each determinand initially was set following assessment of the replies to a

questionnaire and discussion in the NCC. Mr Gardner (WRc) has suggested that these values equate to the threshold values listed in Appendix 2.3.3 (4)(5)(6).

2.3.4   Precision and bias targets were set in early discussion of the NCC. These were largely based on previous experience within WRc's Aquacheck and similar schemes.

For the water column a Total Error Target of 20% (or LOD, whichever is greater) was set; this to be based on a 10% bias allowance and a 10% precision allowance (ie, 2 x standard deviation of 5%).

The exception to this general rule was made for organic compounds. Since experience had indicated that few laboratories could achieve a Total Error Target of 20%, (or LOD), broader levels were initially set - 50% Total Error Target (25% bias, 2 x 12.5% precision).

For sediments and biota, a Total Error Target of 20% (or LOD) was set for metals (10% bias, 2 x 5% precision) and 50% for organics (25% bias, 2 x 12.5% precision).

2.3.5   The "Level of Interest" will be reassessed once NCC has been able to review a collated NMP report. This review should also enable NCC to assess whether participating laboratories are operating at appropriate levels.

2.3.6   Precision and bias targets will be reviewed once the scheme has 'stabilised', ie once the scheme has run for 2-3 years, and an understanding obtained as to what is achievable on a consistent basis by the better laboratories.

2.4   Confidentiality

It was agreed by NCC at the outset that it would be of benefit for progression of the scheme for the results of the exercises to be freely available to all participating laboratories. However, the NCC felt that it was essential that the information remained confidential to the group.

In the Appendices of this report the laboratories are therefore identified by number.

3. MANAGEMENT OF THE AQC SCHEME - FRPB

    3.1   **Scheme Management**

            3.1.1   The UK Marine Pollution Monitoring Management Group (MPMMG)
                    endorsed the need for a national scheme at its 27th meeting. Subsequent
                    discussions resulted in the Forth River Participation Board (FRPB) taking
                    on the task of administering the scheme and its finances on behalf of any
                    consortium, subcontracting by tender for AQC management.   These
                    arrangements have been agreed to continue for year two of the scheme.
                    The role and schedule of work for FRPB are described in Appendix 2.1.3.
                    This section describes the actions and decisions that have been taken in the
                    first year to establish and develop the scheme.

            3.1.2   To date the NCC, as constituted, has met seven times. The schedule of
                    meetings commenced on 18 February 1992 in Edinburgh following an
                    earlier meeting in London during November 1991 at the DoE. Subsequent
                    meetings of the NCC were held on 26 March 1992, 8 June 1992, 4
                    November 1992, 4 February 1993 and 7 May 1993. Two sub-group
                    meetings were held on 29 June 1992 and 28 June 1993, one with the
                    preferred contractor to clarify several technical and practical aspects of the
                    tender specification, prior to letting the contract for year one, the second
                    with QUASIMEME to improve links between the two schemes.

            3.1.3   Day-to-day management of the scheme and its implementation is carried
                    out by the FRPB. Further formal liaison with the contractor takes place
                    through attendance of Water Research Centre (WRc) representatives at
                    NCC meetings. All distributions, reports and one-off exercises in year
                    one have been completed on schedule and within the original contract
                    price.

3.1.4   Reports on the four sample distributions have been issued to all laboratory participants. Feedback is reported to NCC via the WRc and FRPB for subsequent action. Two reports on one-off exercises for nutrients and mercury stability commissioned by NCC have been completed and issued to participants by WRc. An Interim Report on the scheme was presented to the April 1993 meeting of the MPMMG.

3.1.5   Liaison between MPMMG and the NCC is provided by the Chairman of NCC attending one MPMMG meeting per year, as well as through common membership of both groups via Dr C Reid (DoE) and Dr G Topping (SOAFD). Links with the international AQC exercise, QUASIMEME, are provided through Dr D Wells (SOAFD, Project Manager).

3.1.6   During the first year of operation of the scheme the co-ordination of in-house AQC schemes of participating laboratories has commenced. The basic strategy of the scheme, in this respect, has been to gather semi-quantitative and qualitative 'information' from all participants using questionnaires. Three such questionnaires have been issued and responses collated, one on laboratory capability to analyse for determinands, one on marine methodologies and internal AQC status and a third on the intended level of participation for chemical determinands in the NMP. The results of these questionnaires have been integrated into the overall plan and schedule of activities for the scheme, described elsewhere in this report.

3.1.7   The contractor, with the assistance of some laboratory participants, has prepared and provided the required AQC materials for aqueous, sedimentary and biological matrices. The links with QUASIMEME have proved particularly productive in this respect with both MAFF and SOAFD laboratories providing their expertise and resources.

A report on the management of scheme finances is provided in Section 3.4.

3.2 Participation

3.2.1 Participation in the NCC was decided by the MPMMG. The committee has representatives drawn from the National Rivers Authority (NRA), River Purification Boards (RPB), Ministry of Agriculture Fisheries and Food (MAFF), Scottish Office Agriculture and Fisheries Department (SOAFD), Department of Agriculture Northern Ireland (DANI), Department of the Environment (DoE), Department of the Environment Northern Ireland (DOENI) and the British Geological Survey (BGS).

3.2.2 Participation in the AQC Scheme in its first year of operation has embraced principally all those organisations contributing data to the NMP. A full list of the 21 participating laboratories is given in Appendix 3.2.2. Invitations to other organisations to join the scheme, including Universities, Plymouth Marine Laboratory and Institute of Oceanographic Sciences Deacon Laboratory met with a limited response. The level of participation in year two of the scheme is likely to be reduced by three or four laboratories, as a result of their closure.

3.2.3 Invitations to selected UK laboratories to join the QUASIMEME scheme have been issued and accepted by MAFF, SOAFD, Clyde RPB, Forth RPB, Welsh NRA, DOENI and PML. (Appendix 2.2.2). Invitations have been based on past contributions to ICES, JMG, NSTF, OSPARCOM and NMP programmes.

3.3 Contractor Selection

3.3.1 Detailed arrangements for tendering for year one of the scheme were discussed in the Interim Report. The contractor for year one was WRc.

3.3.2 The performance of WRc as the contractor was reviewed at the 6th meeting of the NCC. A number of criteria were considered:

1.   The service provided had given value for money.

2.   Contracted work had been carried out within the contracted prices.

3.   All work had been carried out to schedule and within agreed deadlines.

4.   Customer complaints had been quickly dealt with and were acceptably low.

The unanimous decision at the meeting was that WRc had performed well against these criteria and that the contract for year 2 of the scheme should be awarded to WRc, subject to a satisfactory tender. The contract for year 2 of the scheme has been awarded to WRc commencing 1 July 1993.

3.4   **Financial Arrangements**

3.4.1   Following endorsement of the proposal for a National AQC scheme at the 27th meeting of MPMMG, a 1st year funding consortium of participating laboratories was set up, comprising;

	£
NRA Regions	14,950
RPBs	5,000
MAFF	5,000
SOAFD	5,000
DANI	5,000
DOENI	5,000
DoE	15,000

3.4.2   The DoE's contribution would decrease to a minimum level in subsequent years. It was also decided that allocation of contributions from consortium members to the AQC scheme after year one would be decided by NCC. DoE funding is part of its contribution to the co-ordinated programme of research on the North Sea.

3.4.3   The current financial position of the scheme is healthy. All participating organisations have paid their subscriptions for year one. Taking into consideration the interest on monies received and annual management costs, it is anticipated that the projected outturn for the first year of the scheme will show a small surplus. This surplus will be carried forward to year two of the scheme.

3.4.4   The funding arrangements for year two of the scheme were discussed at the 4th and 5th meetings of the NCC. Various funding arrangements were assessed against the following criteria;

1.   Any scheme should be easy to administer.
2.   Security of funding should be ensured.
3.   The scheme should be seen to be fair.
4.   The scheme should encourage full participation for NMP determinands.

3.4.5   A decision was made at the 5th meeting of the NCC to require participating laboratories to pay a fee of £3500 for year 2. An additional arrangement for laboratories participating at levels up to four groups (see Appendix 2.3.3) determinands was agreed, whereby a fee of £500 per group would be payable. This arrangement would only be available to existing participants and would be reviewed annually. Sufficient funds have been received from participants to ensure the viability of the scheme for year 2.

3.5   **Organisation of Exercises**

3.5.1   The tender document for year one (schedules shown in Appendix 2.3.3) requires the contractor to circulate samples at the following frequency:

Aqueous   Samples   Quarterly

Sediment   Samples   Quarterly

Biota   Samples   Annually

3.5.2   The following schedule of distributions has been implemented in year one;

Distribution No	Distribution Date	Reporting Date	Matrix
1	2 Sept 1992	30 Sept 1992	Aqueous, Sediment
2	25 Nov 1992	23 Dec 1992	Aqueous, Sediment
3	17 Feb 1993	17 Mar 1993	Aqueous, Sediment, Biota
4	26 May 1993	23 June 1993	Aqueous, Sediment

All exercises to date have been carried out on schedule. Returns from laboratories have generally met the deadlines. Only one laboratory failed to make returns in exercises 1, 2, 3 and 4.

3.5.3   A questionnaire issued to all participating laboratories (Appendix 3.5.3) established their intended levels of participation in the distributions. Actual levels of participation are shown in Section 4. The four distributions to laboratories produced comparatively few operational or administrative problems. Those that have arisen have resulted in minor adjustments to the procedures and one improved general guidance note being issued.

3.5.4   A similar approach has been used for year 2 of the scheme, with the levels of participation in the routine distribution by each laboratory being established using a questionnaire approach. Distributions are scheduled for 29 September 1993 and 2 February 1994. (See Appendix 2.2.5).

3.6   <u>One-Off Exercises</u>

During the first year of operation of the AQC scheme two one-off exercises have been completed by the contractor (WRc) on behalf of NCC.   They did not involve a distribution.   These have both covered the stability of chemical solutions containing determinands in the scheme issued by the contractor to participating laboratories. Specifically the exercises have covered "The stability of mixed nutrient spiking solutions" and "The stability of mercury in seawater".   The results of these two studies were described in the interim report (March 1993).

4.0 SUMMARY OF RESULTS FOR YEAR 1 OF THE NATIONAL MARINE AQC SCHEME

4.1 Introduction

4.1.1 The overall scheme has been designed to assess the accuracy and comparability of analytical data produced by individual laboratories monitoring the marine environment, in particular where data is to be used in the NMP.

4.1.2 The first year of the National Marine AQC Scheme consisted of four inter-laboratory tests each of which covered nutrients, metals and organics in water and metals and organics in sediments. One distribution included samples of fish flesh and fish oil for the determination of metals and organics. A summary of the nature of and concentrations in samples distributed in Year 1 is given in Appendix 4.1.2. Each laboratory's performance is summarised for Year 1 in section 4.2 and Appendix 4.1.4 (1-9). These summaries are intended as an indication of the degree of participation in the scheme, together with an outline of performance.

4.1.3 For year 1 the chemical determinands in aqueous, biological and sediment matrices, together with the target concentrations for distributed samples are shown in Appendix 2.3.3. Performance targets are also given in terms of the acceptable bias and precision of the method. These performance targets have been used as the basis for establishing the absolute and percentage error thresholds for each determinand (see Appendix 2.3.3).

4.1.4 In order to evaluate the results of the four distributions of samples it is necessary to derive reference concentrations for the "samples". The reference values used in the programme have been chosen with the aim of providing the best estimate of the true concentration. Wherever possible, reference values have been based on a knowledge of the way samples have been prepared. This usually involved the use of a spiked + residual value. If samples have not been spiked or if the concentration specified as of interest is so low that

a negligible residual could not be assumed, then a consensus value has been used to provide a guide to comparability.

This consensus value has usually been a mean of all laboratories' results after the application of a statistical outlier test (reference 1). In a small number of cases, after careful examination of the data, a reference value has been assigned on the basis of the mean of laboratories' results after the exclusion of discordant (though not necessarily statistically outlying) data. Detailed derivation of reference concentrations are given for each determinand in the Distribution No. 1, 2, 3 and 4 reports.

The results shown in Appendices 4.1.4 (1 to 9) are a summary of both distributions 1, 2, 3 and 4 for the various determinands and matrices. Laboratory performance is assessed on a pass or fail basis against the standards referred to previously. All less than results are treated as not reported.

4.2 Summary of Individual Laboratory's Performance for Year 1

Laboratory 01

Aqueous Determinands

Received samples for estuarine nutrients (sample B only), metals, mercury and all organics. Poor comparability for the nutrients for distributions 1 and 2, but excellent comparability for distribution 4. No data for distribution 3. For the metals, a full set of results reported for distribution 2 but only zinc and chromium for distributions 3 and 4. Positive bias for low concentration samples but good comparability for high concentration sample. No data reported for the metals for distribution 1. For mercury, results for distributions 2 and 4 were satisfactory but no data for distributions 1 and 3. Less than values were reported for HCH for distributions 3 and 4 and HCB

and HCBD for 1, 2 and 3. No data for HCBD and HCB for distribution 4. Good comparability for volatiles and PCP (some less than results reported).

Sediment Determinands

Received sample for metals only. No data for distribution 1. No data for Cr, Hg and As for Distribution 2 and As for distribution 3. All values reported for distribution 4 (except one less than value reported for cadmium). Otherwise good comparability.

Laboratory 02

Aqueous Determinands

Received samples for nutrients for both seawater and estuarine water. No less than values were reported. No data for silicate distribution 2 and TON distribution 4 for seawater sample. Good comparability. Reported problems with having to make large dilutions of test samples. Large positive bias for silicate for distribution 3 (problems with standard solutions used).

Laboratory 03

Aqueous Determinands

Received samples for metals, mercury and organochlorines for distributions 1, 2 and 3. Did not take part in distribution 4. For metals, no less than values were reported and no data for chromium and mercury. Excellent performance for the metals.

Reported data for α-HCH and γ-HCH for Distribution 1 only (negative bias).

Sediment Determinands

Received samples for both metals and organics for distributions 1, 2 and 3 and samples for metals only for distribution 4. Reported less than values for cadmium and no

results for arsenic for all distributions. Otherwise excellent performance for metals. Comprehensive reporting for organics (apart from aldrin and endrin). Initial negative bias for distribution 1, corrected in distributions 3 and 4.

Laboratory 04

Aqueous Determinands

Received samples for all determinands. Reported data for all determinand/sample combinations except for organics for Distribution 1. Improved performance after Distribution 1, where there were initial problems with ammonia and metals. For nutrient determinands (distribution 4) 20 results were reported and only 1 was flagged.

Of 8 results for mercury in Year 1, 6 were flagged. Of a total of 56 possible results for organics, 30 were reported and 8 were flagged.

Sediment Determinands

Received samples for metals. Reported data for all metals except arsenic for Distribution 4. High proportion of flagged data for mercury, arsenic and chromium, otherwise good comparability. (Were sent sample for organics for Distribution 3 - negative bias, but within target for most determinands).

Laboratory 05

Aqueous Determinands

Received samples for nutrients (Groups 1 and 2). Reported data for all determinand/sample combinations except one for TON. Excellent performance, except for ammonia where there is evidence of positive bias; of 8 results for the seawater, 4 were flagged.

Laboratory 07

Aqueous Determinands

Received samples for all aqueous determinands except Group 6; chloroform and carbon tetrachloride. Reported results for all samples except chromium (A and B) all distributions and HCB for Distribution 4. Reported three less than values for TON, lead and mercury Sample A.

Out of a total of 31 results for ammonia and TON, 20 were flagged. Variable performance for trace metals for both low and high levels. Negative bias for the determination of zinc at low concentration. Good comparability for high concentration metal sample for distributions 2 and 4. Excellent performance for mercury distribution 4 for both high and low concentrations. Good performance for pentachlorophenol. Variable accuracy for other organics.

Sediment Determinands

Received sample for metals in sediment. Did not report results for distribution 1 but reported results for all metals except arsenic for distributions 2, 3 and 4. Good agreement between results reported and reference values for most metals. Negative bias of approximately -26% for chromium for all three distributions (results were flagged). Only one other result (lead for distribution 3) was flagged.

Laboratory 08

Sediment Determinands

Received samples for metals and organics. Did not report data for organics for Distribution 1 or for PCBs for Distribution 2. No data for arsenic and less than values reported for cadmium for 3 distributions. Good comparability for metals for Distributions 3 and 4. Of a total of 68 possible results for organic determinands 24 were reported, 9 were flagged.

Laboratory 09

Sediment Determinands

Received samples for metals and organics. For metals a full set of data except for cadmium where less than values were reported. Otherwise good comparability. For organics, data reported only for distributions 1 and 4. Less than values reported for PCB 28, endrin, p,p-DDE and no data for PCBs 31, 101, 105, 156 for distribution 1. No data reported for PCBs 28, 31 and endrin for distribution 4. Variable performance for organics.

Laboratory 10

Aqueous Determinands

Received samples for metals, volatiles and PCP. Almost complete set of data for metals, but poor performance. Less than values reported for cadmium and copper (distribution 1), chromium (distribution 2) and lead (distribution 3), all low concentration samples. Evidence of positive bias (copper and nickel) and negative bias (cadmium, lead and chromium). No data reported for mercury for all distributions. Less than values reported for PCP (distribution 1) for low and high concentration samples and no data for PCP (distribution 2). For volatiles, good comparability for all distributions (did not report for distribution 2). For PCP, moderately good comparability for Distributions 3 and 4.

Sediment Determinands

Received samples for metals only. No less than values were reported. No data for arsenic (all distributions) or for mercury Distribution 4). Good performance.

Laboratory 11

<u>Aqueous Determinands</u>

Received samples for nutrients and all organics. No results reported for nutrients for distributions 1 and 2. No data for silicate for all distributions. Only reported for ammonia and phosphate in distribution 4. Large bias evident for ammonia and variable results for orthophosphate. Less than values reported for PCP (distribution 1) for low and high concentration samples and HCBD (distribution 3) low concentration sample. No data for HCHs (distribution 4) low concentration sample. Otherwise, for organics full set of data of excellent comparability.

<u>Sediment Determinands</u>

Received samples for metals and organics. Reported a full set of data for metals. Good comparability, apart from chromium where there is a clear evidence of positive bias. For organics, no data reported for distributions 3 and 4. In distributions 1 and 2, there were missing data for some PCBs, but otherwise comparability was fair.

Laboratory 12

<u>Aqueous Determinands</u>

Received samples for all determinands. For nutrients a full set of data of excellent comparability was reported (one less than value reported for TON distribution 1). Out of a possible 80 results, 3 were flagged. A full set of data for metals, apart from a less than value reported for zinc in distribution 1. Again, excellent comparability for most determinands. Two less than values reported for mercury for distributions 1 and 2. Otherwise good comparability, particularly for the high concentration sample. Full set of data reported for the organics apart from no γ-HCH for distribution 4. Again, results reported were of good comparability.

Sediment Determinands

Received samples for both metals and organics. Reported a full set of data for metals for all distributions with no less than values. On the whole, good comparability of data; only 6 results out of a total of 32 results were flagged. For organics, less than values were reported for the 'drins for distributions 1 and 2 and no results for distribution 4. PCBs 28, 31, 156, were not reported fully for all distributions (laboratory experienced problems with co-elution of PCB 28 with 31 and p,p-DDT with p,p-DDD). Overall performance was variable and there were instances of serious positive biases.

Laboratory 13

Aqueous Determinands

Received samples for the nutrients in seawater and estuarine samples for distributions 2, 3 and 4. No less than values reported. No data for nitrite for distributions 3 and 4. Problems identified in distribution 2, were overcome in distributions 3 and 4 where comparability was excellent; out of a total of 32 results, none was flagged.

Laboratory 14

Aqueous Determinands

Received samples for nutrients in seawater, organochlorines and PCP. One less than value for silicate for Distribution 4, otherwise a full data set. Good comparability for the nutrients, though some problems apparent with nitrite, particularly at low concentration. No data for organics for Distribution 4, HCBD for all distributions and HCB distribution 3. No data for PCP, apart from Distribution 2. Otherwise comparability was fair.

Sediment Determinands

Received samples for both metals and organics. No data reported for Distribution 4. Less than values for cadmium (distribution 2). Missing data for nickel, chromium and arsenic for distributions 2 and 3. Accuracy of reported values is variable. For organics, full sets of data were reported for Distributions 1 and 2 (apart from aldrin). No PCBs reported for distribution 3. Fairly good comparability for reported data.

Laboratory 15

Aqueous Determinands

Received samples for all groups. Full data set for nutrients apart from two less than values for TON. Excellent comparability for nutrients in both sea and estuarine waters; 5 results were flagged out of a total of 78 results reported.

No values reported for chromium (all distributions), less than values reported for lead for the low concentration sample and two less than values for cadmium. Negative bias for low level zinc. Good comparability for higher concentration samples. Six out of 8 results reported for mercury were less than values.

Complete set of data for the organics, apart from less than value for α-HCH (Distribution 1). No data for PCP (Distributions 2 both samples and 3 high concentration). Excellent comparability except for the organochlorines for distribution 2, where negative bias was evident.

Sediment Determinands

Received samples for both metals and organics. No data reported for metals for any distribution.

For organics, mostly less than values were reported for distribution 1. For distribution 2 serious positive bias for all reported data. For distribution 3 only less than values

reported for PCBs. No data for others. For distribution 4, excellent comparability for a full set of data (no results were flagged).

Laboratory 16

Aqueous Determinands

Received samples for saline nutrients, mercury and organochlorine compounds in seawater. No results for TON Sample B, α-HCH Sample A Distribution 1 or HCBD (distribution 2). Less than value for silicate A (distribution 4). No data for α-HCH for distributions 2, 3 and 4.

Evidence of negative bias for ammonia and TON, otherwise good comparability for nutrients. Of 4 results reported for mercury (plus 2 less than values for distribution 3), 3 were flagged. Of a total of 32 possible results for the organics, 19 results were reported (plus 1 less than value for HCB), 9 were flagged.

Laboratory 17

Aqueous Determinands

Received samples for estuarine nutrients, metals and organics. For nutrients, the only results reported were for nitrite and phosphate (both samples) and ammonia (low sample) for distribution 4 only. Full sets of results for metals were reported for all distributions (apart from chromium for Distributions 2, 3 and 4).

Comparability for metals was good for Distribution 3 but variable elsewhere.

For organics, no data reported for volatiles. Data for organochlorines reported for Distributions 3 and 4, with good comparability. Four results for PCP indicate positive bias.

Sediment Determinands

Received samples for metals only. A full set of data apart from no results for arsenic and only one result for mercury. Evidence of positive bias for chromium. Otherwise good comparability.

Laboratory 18

Aqueous Determinands

Received samples for all groups. For nutrients only two less than values, one for TON and one for nitrite, were reported. Positive bias for ammonia at low concentration. Otherwise excellent comparability; out of a total of 78 results reported for the nutrients only 6 were flagged. Results for metals were reported for distribution 3 and 4 only. Less than values were recorded for cadmium (twice), lead and nickel (once). Variable performance and indication of negative bias. Only one mercury result was reported for distributions 1 and 2. Less than values were reported for distributions 3 and 4. For organics, complete set of results reported with excellent performance. Out of a total of 56 results reported, none was flagged.

Sediment Determinands

Received samples for metals and organics. No less than values. Full set of data for metals, except for arsenic (distribution 2). Good performance, positive bias for cadmium and mercury. For organics, a full set of results was reported. Excellent performance. Out of a total of 68 results, 12 were flagged.

Laboratory 19

Aqueous Determinands

Received samples for all groups. Did not submit results for ammonia (Groups 1 and 2), for the first three distributions and nitrite for Distribution 1. Otherwise,

excellent comparability for nutrients. Out of 61 results reported for nutrients, only 3 results were flagged. One less than value reported for silicate. For metals there were three less than values. No results were reported for chromium., Several results were omitted for Distribution 3. Otherwise good comparability was achieved, particularly for the high concentration sample. Where bias occurred it tended to be negative. For mercury, less than values were reported for both the low and high concentration samples for all distributions.

Excellent performance for organics. (Less than values reported for chloroform for Sample A, and no values for HCBP (all distributions) and PCP for distributions 3 and 4A). Out of 41 results reported, 3 were flagged.

Sediment Determinands

Received samples for both metals and organics. Did not report data for arsenic and reported less than values for cadmium. Completeness for reporting of organics has improved from around 60% in distribution 1 to near to 100% for distribution 4. Performance was excellent for the organics.

Laboratory 20

Aqueous Determinands

Received samples for nutrients (Groups 1 and 2) for distributions 1 and 4. Reported data for all determinand/sample combinations. Reported 3 less than values. Excellent performance, only 2 flagged values (for distribution 4).

Laboratory 21

Aqueous Determinands

Received samples for all determinands except seawater nutrients. For estuarine nutrients, no data have been reported for nitrite. Less than values for TON and

orthophosphate for distribution 2 and orthophosphate for distribution 3. Otherwise good performance. For metals Cd, Cu, Pb reported for both low and high samples (2 less than values for lead low). Only one result reported for zinc, no result for cadmium or chromium. Less than values reported for volatiles (low concentration sample) for all distributions. Complete data set for all organochlorines (except HCBD in distribution 1). Good performance for distribution 4. For PCP, accuracy of reported data is good (but three less than values reported).

Laboratory 22

Aqueous Determinands

Received samples for volatile compounds in seawater. Did not report any results for this year.

4.3 **Summary of Performance**

Appendices 4.3(1) - (4) summarise laboratory performance and participation in the tests in Year 1 of the scheme. Data for nutrients in saline and estuarine samples are included in the summary for 'aqueous nutrients'. Results for trace metals, including mercury, have been summarised in 'aqueous metals'. All organic results have been included in 'aqueous organics'. Similar groupings have been used for sediments and biota. Flagged results correspond to those results that fall outside the error threshold.

4.3.1 **Aqueous Determinands**

For aqueous nutrients determinands, the level of participation and overall accuracy tends to be high. Seven laboratories reported near to the possible maximum of 80 results. The incidence of flagged data was relatively low, at between 5-15%.

In the case of metals in water, there are two main points to be made. Firstly the level of participation is low. Only two laboratories reported over 50

results out of a maximum of 56. Secondly, the incidence of flagged data is higher than for any other determinand/matrix combination.

Performance for aqueous organics is very encouraging. Four laboratories reported over 50 out of a maximum of 56 results. A further 4 laboratories reported 30 plus results. The incidence of important error was low (10-20%). This is impressive at the low concentrations of the test samples. However, it must be borne in mind that a 50% error threshold has been used, compared with 20% for metals and nutrients.

4.3.2 Sediment Determinands

Participation for the metals has been uniformly high and with the exception of a few laboratories, accuracy has been good (incidence of flagged data of 20% or less). Fewer laboratories reported results for organics. Only four laboratories reported greater than 50% of the possible maximum of 68 results. Performance is slightly poorer than for aqueous organics, but the accuracy achieved by two laboratories, which reported a substantial number of results, is encouraging.

4.3.3 Biota Determinands

Appendix 4.3(4) summarises the results from only one distribution. The maximum number of results that could have been reported for metals was 5, and for organics 20. Performance for metals was variable, though the level of participation was high. For organics, participation was limited though three laboratories achieved a very high standard of accuracy.

4.4 Discussion and Conclusions

(a) The four inter-laboratory tests conducted so far provide an illustration of the standard of analytical accuracy which it is possible to achieve in marine monitoring. It is clear from the performance of the best laboratories that it is

possible to produce data of the accuracy required for the NMP.

(b)   For some laboratories, there were clear indications of consistent bias. Apart from the organic determinands there was little suggestion that the techniques used by laboratories were subject to fundamental bias. For organic determinands, errors tended to fall into two categories; consistent negative bias for laboratories which had well controlled analytical systems and large random error for laboratories which could not achieve the required limits of detection.

(c)   **Analysis of Water**

The majority of laboratories achieved the required standard of accuracy for the determination of nutrients over the range of concentrations and sample types distributed. The highest incidences of important error are for ammonia in both sea and estuarine waters. The determination of trace metals in water is often not of adequate accuracy. Problems are often associated with inadequately low limits of detection. In particular, improved methodology appears to be required for the determination of lead, mercury and chromium.

The laboratories may be divided into three roughly equal groups with respect to their determination of organics in water. The first group reported a relatively full set of results with very few important errors. The second group tended to produce results of satisfactory accuracy, but in many instances failed to report results. The third group were subject to large errors and intermittent reporting.

(d)   **Analysis of Sediment**

The comparability of results for the determination of metals in sediments was poor initially, but had improved by distribution 4. This standard of performance was good, particularly given that all laboratories did not use the recommended 'aqua regia' digestion. It is likely that further improvements in comparability can only be achieved if a common digestion procedure is agreed.

Problem metals appear to be chromium, mercury and cadmium at low concentration. Accuracy for the determination of organic determinands in sediments was impressive given the trace concentrations of interest. In laboratories that demonstrate consistent performance there is a tendency towards negative bias, even for the relatively easy to recover spiked determinands used in these exercises. Many laboratories have not been consistent either in frequency of reporting or the accuracy of their results. Four laboratories achieved a standard of performance that was both consistent and high. One laboratory appeared to have serious problems initially, but demonstrated greatly improved accuracy for distribution 4.

(e)   **Analysis of Biota**

From a single distribution it is difficult to draw any firm conclusions about the analysis of fish tissue and oil. There is an indication that performance is similar to that in sediments, possibly with better comparability for organic determinands in oil.

(f)   **Overall Performance**

Overall performance over the four distributions for either a group of determinands in given matrix or for all determinands is shown in Appendix 4.4. The laboratories achieving the highest standard of performance might be regarded as those which combine reported data for a high proportion of determinands, together with the lowest incidence of important error. On the basis of > 60% determinands analysed and reported together with > 80% pass rate on reported data in all four distributions, the following observations can be made.

In the aqueous matrix for nutrients eight laboratories achieved this level of performance, Nos 2, 4, 5, 12, 13, 15, 18 and 19; for metals only laboratory No. 12 achieved this and for organics, 5 laboratories (Nos 7, 11, 12, 18 and 19) achieved this standard of performance. For sediment matrix, six

laboratories (Nos 3, 6, 7, 9, 12 and 19) achieved the standard for metals and only two (laboratories 18, 19) for organics. It would seem unreasonable to draw firm conclusions for biota on the basis of one distribution.

Over all determinands laboratories 12, 15, 18 and 19 demonstrated the best level of performance against the criteria.

4.5 **Future Work, Year 2**

The aim of future quality control activity, both in individual laboratories and on an inter-laboratory basis, should be to assist in controlling error where necessary and to maintain analytical performance at the required level. The programme of inter-laboratory tests for the second year of the Scheme has been designed with two principal aims. Firstly, a demonstration of accuracy and comparability of results for the full range of determinands of interest will be provided by a continuation of the routine inter-laboratory tests. The success of these tests can be measured not only by the standard of accuracy achieved but also by the level of participation. Inter-laboratory tests of this type can only provide a demonstration of participants' proficiency if laboratories continue to report data for as wide a range of determinands as possible. The second aspect of testing in the coming year will be aimed at helping participants improve performance for determinands which have been shown to be subject to poor comparability. For all determinands and matrices, continued attention to the application of routine AQC, involving the development and use of realistic control materials, is essential.

5. MARINE CHEMICAL METHODS AND THEIR PERFORMANCE IN THE NMAQC SCHEME

5.1 Introduction

5.1.1 At the 2nd meeting of the National Co-ordinating Committee (NCC) of the National Marine Analytical Quality Control (NMAQC) Scheme in March 1992 the question of suitable chemical methodologies, to be used in the National Monitoring Programmes (NMP) was discussed. The requirement from the Marine Pollution Monitoring Management Group (MPMMG) was for a text covering suitable methodologies, ranges of detection and quality assured procedures for the determinands in the NMP.

5.1.2 It was agreed that the NCC should undertake this task as part of the NMAQC overall programme but that a "recipe book" approach was incorrect. Instead it was decided that any report should:

- Recommend suitable methods for each determinand or determinand group.
- Recommend AQC procedures for each determinand.

- List the ranges of detection for each determinand/matrix.

At the subsequent 3rd and 4th meetings of the NCC on the 8 June and 4 November 1992, respectively, further discussion of the overall approach and timetable for completion of the task took place. It was concluded that an interim report be submitted to the April 1993 meeting of the MPMMG based principally on information provided by participants in the scheme during 1992/93 and their overall performance in the distributions of test materials.

5.1.3 The approach adopted was to gather suitable information on marine methodologies and to evaluate the performance of these methods against the criteria in the intercomparison distributions.

5.2   Approach

5.2.1   Information on marine methodologies was collected using a questionnaire circulated to all laboratory participants in the scheme during 1992/93. A copy of the questionnaire is shown in Appendix 5.2.1 (1-3).

5.2.2   Responses to the questionnaire were received from most participating laboratories. These responses were discussed in the Interim Report (reference 5).

5.2.3   At the 4th meeting of the NCC it was decided that the performance of a particular chemical method in use in a laboratory should be provisionally assessed on the basis of the results achieved in distributions 1 and 2 of the scheme. The performance results for all four distributions for all laboratories are shown in Appendices 4.1.4 (1-9).

5.3   Marine Methods

5.3.1   The chemical methods reported (Appendix 5.2.1 refers) to be routinely in use in the participating laboratories are shown in Appendices 5.3.1 (1-14), together with associated LODs, operational ranges and internal AQC status. The key for laboratory internal AQC status is given in Appendix 5.2.1. Below, these methods are assessed against their performance in the first two distributions of inter-comparison samples with some account taken of results from distributions 3 and 4. Since only distribution 3 included biota, no detailed examination of methodology has been made at this stage.

5.3.2   Aqueous Nutrients

5.3.2.1   Generally, the standard of accuracy for estuarine and seawater nutrients was met by a large proportion of participating laboratories. A more detailed examination does however point to problems with particular determinands. For example only laboratory 12 was able

to consistently meet the standard for seawater and estuarine ammonia, whereas laboratories 4, 5, 7, 12 and 19 did so for seawater and estuarine orthophosphate. Similar conclusions can be drawn regarding the analyses of other nutrient determinands (see Appendices 5.3.1 (1-5). Their pattern of overall performance was confirmed in the results from later distributions 3 and 4.

5.3.2.2 Both nitrite and silicate analyses carried out by participating laboratories in estuarine and seawater matrices show a high level of achievement of the accuracy standard. For nitrite six laboratories (2, 4, 5, 12, 15 and 18) completed and passed all distributions, and for silicate the comparable number of laboratories is five (4, 5, 7, 12, 15). Whereas only one laboratory, number 19, completed and passed all nitrate distributions. Using the questionnaire responses and the laboratory performance data (Appendices 4.1.4) it is instructive to contrast the level of passes for the two distributions for ammonia with orthophosphate. For both determinands, all laboratories are employing fundamentally the same underlying chemistry in the method, yet the performance for orthophosphate analyses is apparently much better than ammonia. A similar analysis demonstrates that performance of the chemical method employed by participating laboratories for silicate and nitrite against the standard is also good.

5.3.3 Aqueous Trace Metals

5.3.3.1 Copper, Lead, Zinc, Nickel, Cadmium

A similar analysis to that carried out for nutrients reveals that a wide variety of chemical methods are in use to determine aqueous trace metals, including solvent extraction, anodic stripping voltammetry and ICP-MS. No laboratory in the two distributions achieved a 100% pass rate for the five metals, indicating that no one method or

laboratory consistently met the required standard. For particular metals, large variations in limits of detection were reported eg., Cd 5ng/1 to 110 ng/1, probably reflecting the range of environmental concentrations each laboratory routinely encounters. Nevertheless, applying these methods to relatively low concentration analyses produces inconsistent results, it would seem.

5.3.3.2 Mercury

The range of methods in use for determining mercury in aqueous samples is relatively small. Most laboratories are using some form of cold vapour pre-concentration. Again, detection limits that are quoted vary by a factor of about 200, from 1 ng/1 to 200 ng/1. Consequently many less than results are reported by laboratories for low level analyses of distributed samples.

5.3.3.3 Chromium

Only laboratory 4 achieved a 100% pass rate for aqueous analyses of chromium. Only five laboratories reported methodologies. LODs quoted ranged from 20 ng/1 to 1000 ng/1.

5.3.4 Aqueous Organics

5.3.4.1 Chloroform and Carbon Tetrachloride

Most laboratories use a form of purge and trap methodology to determine volatiles in seawater samples. Quoted LODs for all the methods vary by a factor of 4, ranging from 0.05 - 9.2 $\mu g/1$. Performance in the second distribution was marginally better than in the first. Four laboratories achieved a 100% pass rate.

5.3.4.2 Pentachlorophenol

All laboratories use solvent extraction into hexane and derivatization for analysing marine samples. Only laboratories 18 and 17 achieved a 100% pass rate for both exercises. Quoted LODs vary from 1.5 - 200 ng/l, with a wide range of operational values.

5.3.4.3 HCHs. HCB. HCBD

All laboratories appear to be using the same sample treatment of hexane extraction. Some laboratories employ "clean up" when required; GC-ECD/GC-MS is used for quantification and confirmation. Performance against the more relaxed ± 50% standard was good. Laboratories 18 and 19 (ex HCBD) achieved a 100% pass rate. The ranges of LODs quoted are comparatively low, all being typically a few ng/l.

5.3.5 Sediment Metals

A wide range of digestion techniques are currently in use by the participating laboratories, ranging from total analyses using DC arc spectroscopy and HF digests to wet oxidation using concentrated mineral acids. The NCC recommended the use of aqua regia as an "interim" in order to standardise on a technique readily available to all laboratories. A wide range of operational values and LODs were reported, and no laboratory achieved a 100% pass rate for all metals in the scheme.

5.3.6 Sediment Organics

Comparatively few laboratories actually carry out these analyses. The reported methods are very similar, comprising hexane/acetone extraction, silica-alumina "clean-up" separation phase, with ECD-GC/GC-MS quantification and confirmation. Quoted detection limits vary by around an

order of magnitude. Performance, bearing in mind the comparatively low levels in samples, was reasonably good.

The method modifications in use in laboratories are currently being considered by the organics sub-group of the GCSDM. Preliminary observations on improving sampling and analytical matters were presented in the Interim Report.

5.4   **Conclusions and Recommendations**

5.4.1   **Aqueous Nutrients**

On the assumption that the error threshold shown in Appendix 2.3.3 have been correctly set, the chemical methods used by laboratories for orthophosphate, nitrite and silicate can be designated as robust enough to be employed in the NMP with confidence. Greater caution must however be exercised with respect to TON and ammonia. Methods can meet the required standard, but only under an effective control regime.

The expertise to achieve the correct level of performance for individual methods clearly exists within the participating laboratories. The constraints of different instrumentation and operator variability make it impossible to produce a "carbon copy" of the method in every laboratory. Nevertheless it is essential that the good performers transfer their expertise to those that require assistance, if consistent individual laboratory improvements are to be made. Effective ways of doing this have to be found within the Scheme, eg circulation of relevant papers, expert groups, inter-laboratory visits. This approach was thought by NCC to be appropriate for orthophosphate, nitrite and silicate.

However, for TON and ammonia special exercises for all laboratories have been organised for year 2 of the Scheme (see Appendix 2.2.5).

5.4.2 Aqueous Trace Metals (Cu, Pb, Ni, Cd)

The expertise to achieve consistent levels of performance for these analyses does not reside with any one particular laboratory. From the results it seems reasonable to conclude that laboratories should use their present capabilities and resources to improve/reduce LODs and the precision of existing methods. Liaison between participants should be encouraged. In addition special exercises have been organised for year 2 of the scheme.

5.4.3 Aqueous Trace Metals (Mercury)

A similar conclusion is appropriate regarding LODs and precisions for mercury analyses as that for other trace metals. The use of gold trap to pre-concentrate the sample is recommended. Evidence suggests that four laboratories are currently capable of operating at the low level required. Therefore it was considered inappropriate at this time for special exercises to be included in year 2 of the Scheme. Instead a workshop has been organised to address the problem.

5.4.4 Aqueous Trace Metals (Chromium)

Conclusions as for the other trace metals.

5.4.5 Aqueous Organics (Chloroform and Carbon Tetrachloride)

Conclusions as for the trace metals. A strong core of laboratories have consistently met the required performance standards. Their experience should be shared around the participants.

5.4.6 Aqueous Organics (Pentachlorophenol)

Methodologies and technologies are very similar across the participating

laboratories. A small core of laboratories consistently met the standard. Their experience should be shared across the group.

5.4.7 Aqueous Organics (HCHs, HCB, HCBD)

Generally performance against the required standard was good. Laboratories are customarily all using the same methodology. Results are encouraging. In addition special exercises have been organised for year 2 of the Scheme.

5.4.8 Sediment Metals (Cu, Pb, Ni, Cd, Cr, Hg, As)

Generally performance against the required standard was inconsistent. Laboratories use a wide range of digestion techniques to determine these trace metals. Until agreement is reached on the preferred methodology little improvement can be expected. Methodologies for "Aqua Regia" and total digests should be described and agreed by NCC as a priority.

5.4.9 Sediment Organics (PCBs, Drins, DDTs, HCB)

Generally performance against the required standard was good. Improvements in methodologies should be pursued in concert with the organics sub-group of the GCSDM.

5.4.10 Biota Metals and Organics

Only one exercise (Distribution 3) included biota. It was felt unreasonable to draw firm conclusions on the basis of one distribution. NCC has decided that in order to achieve sufficient data, biota will be included in both distributions in year 2 of the scheme, and more than 1 sample in each distribution. Special exercises for metals and organics in both sediment and biota are envisaged for year 3 of the scheme. In addition data will become available from year 1 of QUASIMEME.

6. CONCLUSIONS AND RECOMMENDATIONS ON FUTURE STRATEGY

A National Marine AQC scheme has been established; this scheme encompasses approximately 80% of the determinands listed in NMP. Those determinands not included are mainly field determinands, although some were excluded because of likely insufficient participation.

The results of the four exercises indicate that the overall performance was good in relation to that achieved in similar inter-laboratory exercises for water analysis, especially if the low concentrations of interest are considered.

For some aqueous determinands, eg silicate, nitrite and orthophosphate, the required standard of accuracy was met by a large proportion of participants. However, improved accuracy appears to be required in many instances for trace metals in water and in some laboratories for organic determinands (here there are some laboratories who appear to consistently meet the required standards).

The four exercises indicate that comparability for both metals and organics in sediment and biota was not adequate; in some instances very significant variation from the mean/true value were recorded.

Recommendations have been made to all participants concerning the analytical range/limit of detection and the requirements to ensure adequate in-house AQC procedures.

Information has been circulated to participants to assist in trouble shooting problems.

Proposals for in-house AQC have been drafted and should be adopted as policy at the next NCC meeting.

A review is being undertaken of the quality aspects of sampling and sample handling. The findings of this review will be circulated to all participants, with the aim of controlling these significant sources of error.

Links of NCC to QUASIMEME have been explored; use of materials prepared for within the National Marine AQC scheme should commence in 1994. This link should provide useful feedback on problems relating to the analysis of organics and metals in sediment and biota by late 1994, and reduce duplication of effort.

It is tentatively concluded that analytical methods exist which will produce adequate nutrient data for NMP. These methods have been adapted to work with success using a variety of equipment. However, these same chemistries have also been used by some laboratories who have failed to achieve the required standards. This tends to confirm that the use of a standard method alone would not give adequate data - this will only be achieved if the method is applied as part of a system under quality assured conditions. NCC will endeavour, through dissemination of information and special exercises, to ensure that overall performance improves to that currently achieved by the better laboratories.

A contract has been established with WRc for the second year of operation of the scheme.

Funding for the second year of the scheme has been secured. These funding arrangements are even handed and have been designed to encourage full participation whilst allowing for a minimal level of participation for those laboratories analysing a small number of NMP determinands.

The choice of levels of interest and precision and bias targets was an essentially pragmatic one - a compromise to establish the overall AQC scheme as quickly as possible and to gain information on which further judgement could be made. As the results of the first exercises are reviewed it may be necessary to amend the precision and bias targets. Similarly, a review of the NMP data might indicate more appropriate levels of interest and should confirm the level at which each laboratory should be operating. It is probable that some of the targets will be modified to reflect what is currently achievable by the better laboratories.

The list of determinands for inclusion in the scheme will be reviewed (i) as information is gathered from the initial exercises (ii) in the light of changes to NMP. The second year of the scheme reflects proposed changes to NMP - thus organophosphorus pesticides, triazine herbicides and additional volatiles have been added for estuarine samples.

The structure of the scheme for second and subsequent years has been reviewed. A scheme of similar structure and extended scope to that operational in year one is to be continued for subsequent years - but at a reduced frequency of two routine distributions per year. This will allow for continued assessment of laboratory performance to be made. The scheme will diversify to allow for special exercises to target problem areas, ie in year two the problem areas to be addressed are (1) ammonia and TON in aqueous samples, trace metals (not Hg) in aqueous samples, and organochlorine insecticides in aqueous samples. In addition, workshops will be held to address particular problems eg mercury in aqueous samples.

A check in the provision of data for NMP purposes is being performed to ensure that this data has been subject to the rigors of the Marine AQC scheme; all data provided for NMP purposes not subject to the scheme should be flagged.

It is further recommended that in due course data failing this meets the specified quality standards be subject to a separate flag.

7.   DEFINITIONS AND EXPLANATIONS OF TERMINOLOGY

The purpose of Analytical Quality Control (AQC) exercises is to ensure that analytical performance is within the statistical variation set. To determine these errors, measurements of precision and bias are made. .

In the statistical calculations made on the results it has been assumed that the distribution of random errors follows the normal (Gaussian) distribution. This allows prediction of the expected magnitude of the analytical errors from the standard deviation of the results.

Terms used in Precision and Bias Calculations

Below are brief explanations of the terms used in the AQC precision and bias calculations. A fuller discussion can be found in Water Research Centre NS30 'Manual on Analytical Quality Control for the Water Industry' (Reference 1).

Batch of Analysis

An operational term used to refer to a series of determinations which have been made on a single occasion or under broadly similar experimental conditions. A batch is usually taken to refer to analysis for which a given calibration applies.

Precision

The degree of agreement existing between repeated measurements on the same sample made under special conditions. Precision of results (or rather lack of it) is usually expressed in terms of standard deviation).

Bias

Systematic error - a consistent difference between the mean of many results and the true value.

Total Error or 'Accuracy'

This is a combination of the precision and bias errors and is the total error on an analytical result. It is not strictly possible to add random and systematic components of error (one measured in absolute units and the other being standard deviation-based), but an estimate of the maximum error can be obtained from a linear combination. If the normal precision and bias targets of 5% relative standard deviation and 10% bias are taken, the total error on any one result could be 20% (10% from the random errors and 10% bias).

Control Sample

A sample which is analysed for quality control purposes.

Level of Interest

The concentration or value which is used as an assessment of analytical results. The level of interest usually corresponds to a statutory limit value or 10 times the required Limit of Detection.

Total Standard Deviation

The standard deviation of individual results selected at random from any batch of analysis. Total standard deviation comprises components of both within and between batch random error; it is intended to be a measure of all the elements of random error which might affect the results.

Within-batch Standard Deviation

The standard deviation of results obtained by replicate determinations in single batch of analysis. It is a measure of short-term random error.

Between-batch Standard Deviation

The standard deviation of results obtained by replicate determination in different batches of analysis. It is a measure of longer-term random error.

Statistical Control

The condition where sources of random error affecting analysis are consistent. When a state of statistical control is achieved the measurement process can be thought of as stable, predictable and free from unexpected sources of error.

Test Control

A sample analysed for purposes other than analytical quality control.

Limit of Detection

Limit of detection should be estimated by following the guidance giving in NS30. In summary LOD is based on 4.65 σ_w, where σ_w is the within batch standard deviation of blank determinations. An estimate of σ_w, S_w, is obtained in the precision tests. The factor 4.65 corresponds to 2.2t, where t is the value for the student's t statistic for the chosen probability level of 0.05 and an infinite number of degrees of freedom. The value for t used in practice should be modified accordingly to the number of degrees of freedom associated with S_w. For example, with 11 degrees of freedom LOD is 5.1 S_w.

REFERENCES

1.   Cheeseman, R E Wilson revised by Gardner M J 1989 - A Manual on Analytical Quality Control for the Water Industry - WRc Report no. NS30.

2.   Kirkwood J, Personal Communication to A H Griffiths (FRPB)

3.   ACMP 1989 Report (ICES 1989).

4.   National Marine AQC Scheme - Marine Methods Report in Preparation.

5.   Interim Report on the National Marine Analytical Quality Control Scheme 1992/93. Dr M A Jessep and Dr A Griffiths.

NATIONAL MARINE ANALYTICAL QUALITY CONTROL SCHEME
NATIONAL CO-ORDINATING COMMITTEE (NCC)
ATTENDANCE AT 6TH MEETING

Dr M Jessep	(NRA Anglian)	Chairman
Dr A Griffiths	(Forth RPB)	Scheme Manager
Mr G Firth	(NRA Yorkshire)	
Dr A Kelly	(SOAFD)	
Mr I King	(DoENI)	(IRTU)
Mr R Law	(MAFF)	
Mr T Long	(NRA HQ Bristol)	NRA Representative
Dr D Miles	(BGS)	
Mr B Miller	(Clyde RPB)	RPB Representative
Dr S Mitchell	(DANI)	
Dr M Roberts	(DoE)	Secretary
Dr D Wells	(SOAFD)	Project Manager QUASIMEME

ROLE OF THE NATIONAL CO-ORDINATING COMMITTEE (NCC)

The functions and role of the National Co-ordinating Committee for the national marine AQC scheme are as follows:-

- Define what services are required

- Interact with FRPB as managers of the contract.

- Review other organisations/laboratories that should be approached to join the scheme.

- Agree and set an annual budget and itemise contributions from individual participants.

- Assess the funding requirements of FRPB to service the scheme and the NCC.

- Develop all necessary definitions.

- Develop and document an overall plan for the scheme.

- Receive and review reports from participating laboratories on any problems arising from internal and external AQC exercises.

- Receive and review reports from the FRPB on the management of the scheme.

- Establish the frequency and location of committee meetings.

- Receive and review reports from the tendering organisation on AQC exercises.

- As necessary, establish ad-hoc groups to address problems as they arise and provide members to chair each sub-group.

- Produce an annual report, which will be presented to MPMMG and DoE for information.

- Establish links and stimulate collaboration with international inter-comparison exercises.

- Encourage NAMAS accreditation and co-ordinate in-house AQC policy.

- Make recommendations and receive reports from participating laboratories on in-house AQC.

- Establish a timetable and dates for reports.

ROLE OF THE FORTH RIVER PURIFICATION BOARD

OBJECTIVES

1. To establish a managed national marine analytical quality control scheme.

2. To co-ordinate the in-house AQC policy of participating organisations on a national basis.

3. To recommend and, where necessary, produce appropriate quality materials.

4. To manage the schemes finances.

SCHEDULE OF WORK

1. Provide secretarial and operational support for the National Co-ordinating Committee.

2. Implement the plan for the national AQC Scheme.

3. Audit and report to the Committee on the planned work programme.

4. Receive and manage funds donated by participating members of the AQC consortium.

5. Co-ordinate with the Committee the content of the tender document, put it out to relevant laboratories, evaluate tenders, provide a report with recommendations to the NCC and set the contract.

REPORTS

Provide progress reports to the NCC for each meeting with a longer and fully documented annual report. Every publication from the work should acknowledge all consortium contributors.

Analytical Requirements

Determinand		Code	UW	FW	SS	SF	FM	FL
Metals								
Al	(Aluminium)	AL	-	-	mg/kg	-	-	-
Hg	(Mercury)	HG	-	ng/l	µg/kg	mg/kg	mg/kg	-
Cd	(Cadmium)	CD	-	ng/l	µg/kg	mg/kg	-	mg/kg
Cu	(Copper)	CU	-	µg/l	mg/kg	-	-	-
Pb	(Lead)	PB	-	µg/l	mg/kg	mg/kg	-	mg/kg
Ni	(Nickel)	NI	-	µg/l	mg/kg	-	-	-
Zn	(Zinc)	ZN	-	µg/l	mg/kg	mg/kg	-	-
As	(Arsenic)	AS	-	-	mg/kg	-	mg/kg	-
Cr	(Chromium)	CR	-	µg/l	mg/kg	-	-	-
TBT	(Tributyl tin)	TBTIN	ng/l	-	µg/kg	mg/kg	-	-
[in conjunction with Dogwhelk survey - See paragraph 8]								
Organic Compounds								
PCB	(Polychlorinated biphenyls)	CB28,CB52,etc	-	-	µg/kg	µg/kg	-	µg/kg
	[congeners: 28,52,101,105,118,128,138,153,156,170,180] [1]							
α-HCH	(Alpha-hexachlorocyclohexane)	HCHA	ng/l	-	-	µg/kg	-	-
γ-HCH	(Gamma-hexachlorocyclohexane: Lindane)	HCHG	ng/l	-	-	µg/kg	-	-
Dieldrin	*[Unfiltered Water: estuarine sites only]*	DIELD	ng/l	-	µg/kg	µg/kg	-	µg/kg
Aldrin	*[estuarine sites only]*	ALD	ng/l	-	µg/kg	µg/kg	-	µg/kg
Endrin	*[estuarine sites only]*	END	ng/l	-	µg/kg	µg/kg	-	µg/kg
HCB	(Hexachlorobenzene)	HCB	ng/l	-	µg/kg	µg/kg	-	-
PCP	(Pentachlorophenol)	PCP	ng/l	-	-	µg/kg	-	-
DDT	(Dichlorodiphenyltrichloroethane)	TDEPP,DDEPP DDTPP	-	-	µg/kg	µg/kg	-	µg/kg
	[pp TDE, pp DDE, pp DDT]							
HCBD	(Hexachlorobutadiene) *[estuarine sites only]*	HCBD	ng/l	-	-	µg/kg	-	-
[Priority Hazardous Substances to be analysed on Unfiltered Water								
samples at estuarine sites only -	*See Table 1a]*		µg/l	-	-	-	-	-
PAH's	(Polycyclic aromatic hydrocarbons) *[See Table 1b]*		-	-	µg/kg	µg/kg	µg/kg	-
[Part of Special Survey of Additional Determinands - See paragraph 8]								
Nutrients etc								
NH₄ - N	(Ammonium)	AMON	-	mg/l*	-	-	-	-
NO₃ - N	(Nitrate)	NTRA	-	mg/l*	-	-	-	-
NO₂ - N	(Nitrite)	NTRI	-	mg/l*	-	-	-	-
PO₄ - P	(Orthophosphate)	PHOS	-	mg/l*	-	-	-	-
SiO₄ - Si	(Silicate)	SLCA	-	mg/l*	-	-	-	-
Dissolved Oxygen		DOXY	mg/l†	-	-	-	-	-
Suspended solids		SUSP	mg/l	-	-	-	-	-
Chlorophyll a		CPHL	µg/l	-	-	-	-	-
Physical Measurements								
Secchi depth or other appropriate measurement		SECCI	m	-	-	-	-	-
Salinity		*[See Table 1c]*	‰	-	-	-	-	-
Temperature		TEMP	°C	-	-	-	-	-
Oyster Embryo Bioassay								
Percent net response		PNR	%	-	%	-	-	-

[1]   Also Congeners 77, 126 and 169 if possible.

Alternative units: Chemical measurements can alternatively be given as required by ICES,
ie as g/l (* = moles/l; † = l/l) or g/g in scientific notation expressed in the form: x.xxxxExxx

Code: ICES Parameter/Contaminant Code, to be used as determinand identifier when recording data.

UW: Unfiltered water
FW: Filtered water - pore size 0.45 microns
SS: Total Surficial Sediment - Total analysis of <2000 µm fraction of sediment; dry weight
SF: Shellfish - wet weight (plus % solid and % lipid)
FM: Fish Muscle - wet weight (plus % solid and % lipid)
FL: Fish Liver - wet weight (plus % solid and % lipid)

PARTICIPATION IN OUASIMEME

Participating Organisation	Determinands
1. Department of Economic Development Industrial Science Centre (DOENI)	Organics, Metals, Nutrients
2. Plymouth Marine Laboratory	Organics, Metals, Nutrients
3. Clyde River Purification Board	Organics, Metals, Nutrients
4. NRA Welsh Region	Organics, Metals, Nutrients
5. SOAFD	Organics, Metals, Nutrients
6. MAFF, Burnham on Crouch	Metals, Organics
7. MAFF, Lowestoft	Nutrients
8. Forth River Purification Board	Organics, Metals, Nutrients

International
Marine AQC Exercises
Quasimeme
ICES

National Marine
AQC Scheme

In-house AOC

Existing In-
house systems

YEAR 1

Review

Revision of
Systems

Special
Exercise

Scheme

Continuous
Activity

YEAR 2

YEAR 3

Links
between
activities

Indicates an exercise

Indicates
modification to
scheme.
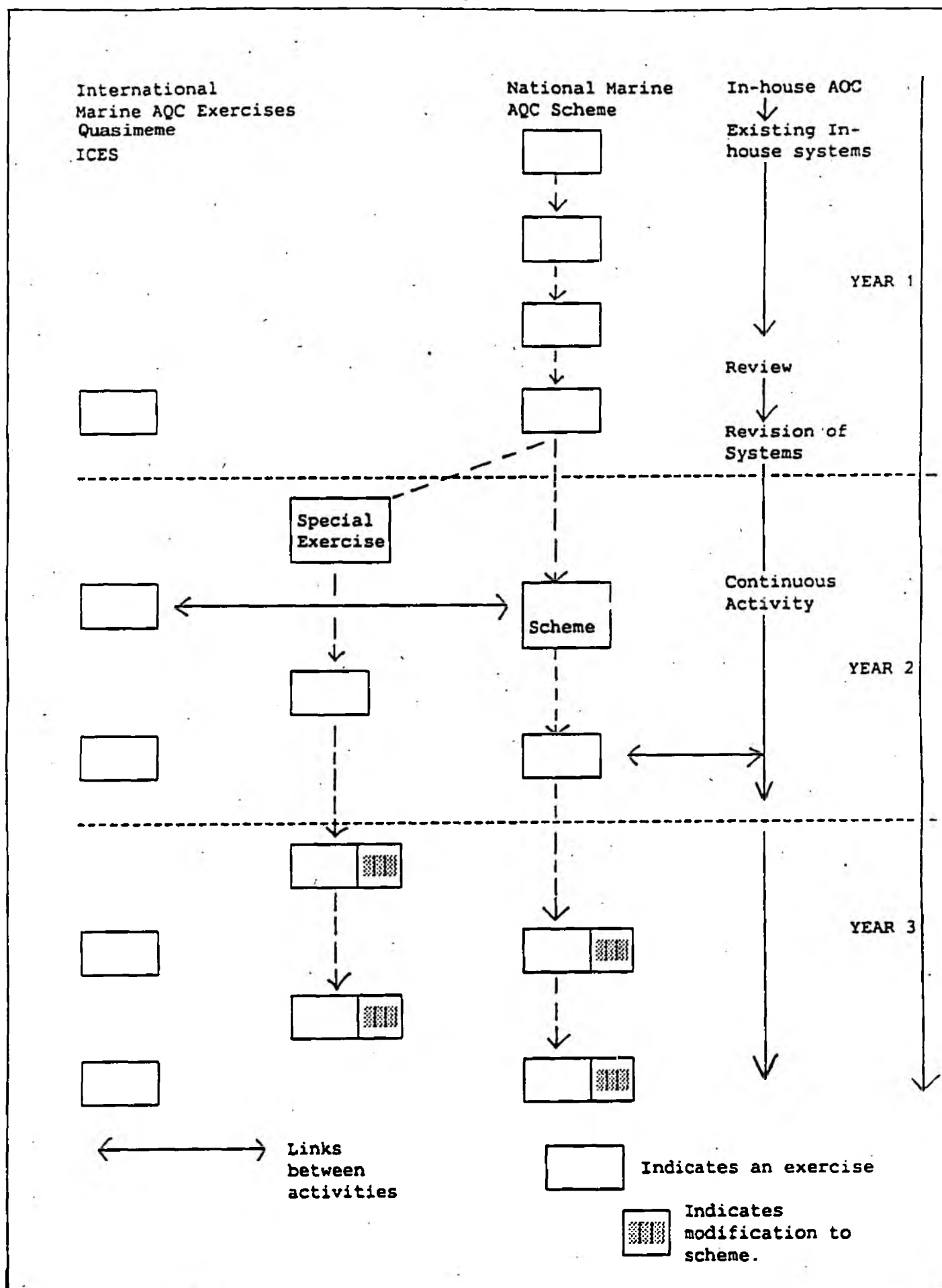
NATIONAL MARINE AQC SCHEME
JULY 1993/JUNE 1994

DETERMINAND GROUPS

TABLE 1

Aqueous Determinands (Samples at both low and high concentrations will be provided)

Two Distributions per year

GROUP 1	Determinand	Units
	Ammonia	μM
	TON	μM
	Nitrite	μM
	Orthophosphate	μM
	Silicate	μM

Sample size - 2 litres of filtered, stabilised, unpreserved seawater for low concentration Sample A and 2 litres for high concentration Sample B. Spiking solutions (30 ml) will also be provided for ammonia, TON, nitrite and orthophosphate.

GROUP 2 **		
	Ammonia	μM
	TON	μM
	Nitrite	μM
	Orthophosphate	μM
	Silicate	μM

Sample size - 2 litres of filtered, stabilised, unpreserved estuarine water (salinity approx. 5 ‰) for low concentration Sample A and 2 litres for high concentration Sample B. Spiking solutions (30 ml) will also be provided for ammonia, TON, nitrite and orthophosphate.

GROUP 3		
	Dissolved Cadmium	μg/l
	Dissolved Copper	μg/l
	Dissolved Lead	μg/l
	Dissolved Nickel	μg/l
	Dissolved Zinc	μg/l
	Dissolved Chromium	μg/l

Sample size - 1 litre of filtered seawater for low concentration Sample A and 1 litre for high concentration Sample B (each preserved with 0.2% nitric acid).

GROUP 4	Dissolved Mercury	ng/l

Sample size - 1 litre of filtered seawater for low concentration Sample A and 1 litre for high concentration Sample B (each preserved with 0.6% nitric acid).

TABLE 1 - CONTINUED

GROUP 5	Determinand	Units
	α-HCH	ng/l
	γ-HCH	ng/l
	HCB	ng/l
	HCBD	ng/l
	β-HCH	ng/l
	Dieldrin	ng/l
	Aldrin	ng/l
	Endrin	ng/l
	Isodrin	ng/l
	p,p–DDT	ng/l
	·p,p–DDE	ng/l
	p,p–DDD	ng/l
	o,p–DDT	ng/l
	Trifluralin	ng/l
	Total Endosulphan··	ng/l
	1,2,4 trichlorobenzene	ng/l
	1,3,5 trichlorobenzene	ng/l
	1,2,3 trichlorobenzene	ng/l

Sample size - 2 litres of filtered, unpreserved seawater for low concentration Sample A and 2 litres for high concentration Sample B. Two spiking solutions in methanol (7 ml) will also be provided.

GROUP 6		
	Chloroform	µg/l
	Carbon Tetrachloride	µg/l
	Trichloroethane	µg/l
	1,2 Dichloroethane	µg/l
	Trichloroethene	µg/l
	Tetrachloroethene	µg/l

Sample size - 2 litres of filtered, unpreserved seawater for low concentration Sample A and 2 litres for high concentration Sample B. Two spiking solutions in methanol (7 ml) will also be provided.

GROUP 7		
	Pentachlorophenol	ng/l

Sample size - 2 litres of filtered, unpreserved seawater for low concentration Sample A and 2 litres for high concentration Sample B. Two spiking solutions in methanol (7 ml) will also be provided.

TABLE 1 - CONTINUED

<u>GROUP 8</u> (New Group)

Determinands	Units
Simazine	ng/l
Atrazine	ng/l

Sample size - 2 litres of filtered, unpreserved seawater for low concentration Sample A and 2 litres for high concentration Sample B. Two spiking solutions in methanol (7 ml) will also be provided.

<u>GROUP 9</u> (New Group)

Azinphos-methyl	ng/l
Fenthion	ng/l
Malathion	ng/l
Parathion	ng/l
Parathion-methyl	ng/l
Fenitrothion	ng/l

Sample size - 2 litres of filtered, unpreserved seawater for low concentration Sample A and 2 litres for high concentration Sample B. Two spiking solutions in methanol (7 ml) will also be provided.

All groups except group 2   = Full seawater salinity

** Group 2   = Salinity = 5‰

Performance Targets;

(1)   For Groups 1,2,3 and 4: 20% Total Error @ 10% Bias, 10% Precision

(2)   For Groups 5,6,7,8 and 9: 50% Total Error @ 25% Bias, 25% Precision

NATIONAL MARINE AQC SCHEME - SEDIMENT DETERMINANDS

TABLE 2

Two distributions per year

GROUP 1	Determinand	Units
	Copper	mg/kg
	Lead	mg/kg
	Cadmium	mg/kg
	Zinc	mg/kg
	Nickel	mg/kg
	Chromium	mg/kg
	Mercury	mg/kg
	Arsenic	mg/kg
	Aluminium	%
GROUP 2	HCB	µg/kg
	PCB 28	µg/kg
	PCB 31	µg/kg
	PCB 52	µg/kg
	PCB 101	µg/kg
	PCB 105	µg/kg
	PCB 118	µg/kg
	PCB 138	µg/kg
	PCB 153	µg/kg
	PCB 156	µg/kg
	PCB 180	µg/kg
	Aldrin	µg/kg
	Endrin	µg/kg
	Dieldrin	µg/kg
	Isodrin	µg/kg
	p,p—DDT	µg/kg
	p,p—DDE	µg/kg
	p,p—DDD	µg/kg
	o,p—DDT	µg/kg

Sample size - 25 g of a dried, sieved (63 µm) marine sediment will be provided for Group 1. Two portions of a dried sieved (63 µm) sediment as specified by the laboratory will be provided for Group 2.

Performance Targets

(1) For Group 1: 20% Total Error @ 10% Bias, 10% Precision

(2) For Group 2: 50% Total Error @ 25% Bias, 25% Precision

NATIONAL MARINE AQC SCHEME - BIOTA

TABLE 3

Two distribution per year (three samples of fish tissue will provided for Distribution 6 and three of oil for Distribution 5, otherwise one sample of each type for each distribution).

GROUP 1	Determinand	Units
	Lead	mg/kg
	Cadmium	mg/kg
	Zinc	mg/kg
	Mercury	mg/kg
	Arsenic	mg/kg
GROUP 2	Dieldrin	µg/kg
	Isodrin	µg/kg
	α-HCH	µg/kg
	γ-HCH	µg/kg
	β-HCH	µg/kg
	p,p–DDT	µg/kg
	p,p–DDE	µg/kg
	p,p–DDD	µg/kg
	o,p–DDT	µg/kg
	aldrin	µg/kg
	endrin	µg/kg
	HCB	µg/kg
	HCBD	µg/kg
	PCB 28	µg/kg
	PCB 31	µg/kg
	PCB 52	µg/kg
	PCB 101	µg/kg
	PCB 105	µg/kg
	PCB 118	µg/kg
	PCB 138	µg/kg
	PCB 153	µg/kg
	PCB 156	µg/kg
	PCB 180	µg/kg
GROUP 3	PCP	µg/kg

Sample size - 5g of each freeze-dried fish tissue for Group 1 and 5g of each fish oil for Groups 2 and 3.

Performance Targets

(1) For Group 1: 20% Total Error @ 10% Bias, 10% Precision

(2) For Groups 2 and 3: 50% Total Error @ 25% Bias, 25% Precision

SUMMARY PROGRAMME FOR THE NATIONAL MARINE AQC SCHEME 1993/1994

1. Introduction

It is intended that the scheme should satisfy two aims:

a)   to provide a continuing check on comparability for the full suite of determinands and matrices required for marine analysis;

b)   to assist participating laboratories in achieving the improvements in performance where accuracy falls short of that required.

The proposed approach is outlined below.

2. Routine distributions

The continuing check on comparability would comprise two distributions (Nos 5 and 6, in September 1993 and February 1994, respectively) of the kind carried out in year 1. Additional features of these exercises would be:

(a)   inclusion of more biota samples to provide a more detailed summary of performance in this matrix - to form the basis of a future programme of work);

(b)   addition of further organic determinands to all three matrices - to cover Annex 1 of the Dangerous Substances Directive, e.g. 'drins, volatiles, DDTs, trichlorobenzenes, triazines and organophosphorus compounds for water analyses and less extensive additions for sediments and biota;

(c)   determination of aluminium in sediment.

3. Intensive Exercises

The programme of improvement will be directed towards determinands which have been shown to be subject to inadequate accuracy and poor comparability. The following determinands are suggested for year 2. A schedule of actions is given below.

(a)   Ammonia and TON in sea and estuarine waters. ⁻

(b)   Cadmium, chromium, lead, and zinc in seawater (any interlaboratory tests would include copper and nickel). Mercury would be approached separately.

(c)   Organochlorine determinands in seawater

The basic approach is one of reviewing the likely sources of poor comparability and examining existing performance data. This is followed by an interlaboratory test involving a range of test samples, chosen with the aim of identifying different types of analytical error, and on the basis of the results making recommendations to participants.

The emphasis would be modified according to the likely sources of error and the best way in which these might be controlled. For example, in the case of nutrients in seawater, the key areas of blank correction and the effect of salinity would need to be examined; in the case of metals in seawater a more general appraisal of performance would be required.

TIMETABLE

Ammonia and TON

July 1993	digest of recommendations on methodology
August 1993	distribution of ten test samples to examine effectiveness of calibration and blank correction for samples of different salinity.
October 1993	summary of performance and recommendations

Metals in Seawater

October 1993	Review of methods and performance (precision and recovery) information available from participating laboratories
November 1993	Distribution of eight test samples to examine effectiveness of calibration and blank correction for samples of different salinity.
January 1994	Distribution of further test samples to confirm improved accuracy.

Organochlorine Compounds in Seawater

October 1993	Review of methods and performance (precision and recovery) information available from participating laboratories
November 1993	Distribution of six 'standards' as a check on calibration and recovery.
March 1994	Distribution involving real samples.

NATIONAL MARINE AQC SCHEME (July 1993 - June 1994)

A) Routine Distributions

DISTRIBUTION NUMBER	DISTRIBUTION DATES	REPORTING DATE
5.	29 September 1993	29 October 1993
6.	2 February 1994	4 March 1994

B) Special Exercises

DISTRIBUTION	DISTRIBUTION DATES	REPORTING DATE
Ammonia and TON in Water	11 August 1993	10 September 1993
Trace metals in water (not Hg)	9 November 1993	13 December 1993
O/Cl Compounds in water	9 November 1993	13 December 1993
Trace metals in water (not Hg)	19 January 1994	25 February 1994
O/Cl Compounds in water	30 March 1994	6 May 1994

MATRIX

AQUEOUS SAMPLES	SEDIMENTS	BIOTA
AQUEOUS SAMPLES	SEDIMENTS	BIOTA

10 Saline water samples / standards

8 test samples

6 test samples

Follow-up to
previous exercise

Follow-up to
previous exercise

DOCUMENTATION CIRCULATED TO PARTICIPANTS
IN THE NMAOC SCHEME IN YEAR 1

Reports   1   Distribution 1 Report

                     2   Distribution 2 Report

                    .3   Distribution 3 Report

                     4   Distribution 4 Report including Summary

                     5   Interim Report to MPMMG

                     6   Draft Report on Marine Chemical Methods

                     7   Draft Report on In-house AQC

Questionnaires: 1   National Marine AQC Scheme: Marine Methods

                     2   National Marine AQC Scheme: Participation Year 1

                     3   National Monitoring Programme: Participation Year 1

Information/Papers: 1   Stability of Mercury in Inter-laboratory Tests for Marine Samples.

                     2   Quality Assurance of Information in Marine Environmental
                              Monitoring Programme: An Introduction to QUASIMEME

                     3   Quality Control in Marine Benthic Studies

                     4   Provisional Method for Particular Organic Carbon in Marine Water
                              by CHN Analyser.

5   ACMP Report (ICES 1989) Studies of Contaminants in Sediments
        Normalisation Techniques: Section 14, Coop Res Rep 167.

6   Tests to check Stability of Mixed Nutrient Spiking Solutions.

7   Loring D H and Rantala (1988): Mar Chem, 24, 13-28. Reports of
        the ICES inter-comparison exercise which conducted comparisons of
        four different dissolutions/extractions procedures, including total
        digestion.

8   Report of the ICES Advisory Committee on Marine Pollution 1992.
        ICES Co-op Res Rept No. 190.   Quality Assurance of Marine
        Sampling.

9.   Kirkwood, D Nutrients: Practical Notes on their Determination in
        Seawater. (In press).

10.   GCSDM Sub-group Paper on Analytical Procedure for Organics.

CURRENT NAMAS/BS 5750 STATUS

Organisation	Region/Laboratory	Status
NRA	Severn Trent	)
	Welsh	)
	Yorkshire	)
	Anglian	) Accredited
	North West	)
	Thames	)
	Northumbria	)
	South West	)
	Southern	)
IRTU		Accredited (also BS 5750 achieved)
DANI		)
MAFF		)
SOAFD		) Under active review
RPB's	Clyde	) and consideration
	Forth	)
	Highland	)
	Tay	)
	Solway	)

UK MARINE ANALYTICAL QUALITY CONTROL

AQUEOUS DETERMINANDS (μgl^{-1} except where stated)

Determinand	Sample	Spike	
Group 1			
Ammonia μm	5	20	
Nitrate/TON μm	5	25	
Nitrite μm	0.5	5	
Orthophosphate μm	0.5	3	
Silicate μm	5	15	
** Group 2			
Ammonia μm	20	100	20% Total Error at 10% Bias
Nitrate/TON μm	15	100	
Nitrite μm	2	10	
Orthophosphate μm	5	10	
Silicate μm	20	100	
Group 3			
Dissolved Cadmium	0.05	0.2	
Dissolved Copper	0.5	2	
Dissolved Lead	0.2	2	
Dissolved Nickel	0.5	2	
Dissolved Zinc	2	10	
Group 4			
Dissolved Chromium	2	2	
Group 5			
Dissolved Mercury ng.1^{-1}	5	20	
Group 6			
α HCH ng.1^{-1}	2	10	
γ HCH ng.1^{-1}	2	10	
HCB ng.1^{-1}	2	10	
HCBD ng.1^{-1}	5	10	
	2		
	5		
Group 7			
Chloroform	0.1	2	50% Total Error at 25% Bias
Carbon Tetrachloride	0.1	2	25% Precision
Group 8			
Pentachlorophenol ng.1^{-1}	25	125	

All groups except group 2 = Full sea water salinity   ** Group 2 = Salinity = 5

UK MARINE ANALYTICAL QUALITY CONTROL
SEDIMENT DETERMINANDS (mg.kg^{-1} dry wt)

Determinand	Range	Performance Targets
Group 1		
Copper	10-100	
Lead	20-100	
Cadmium	0.5-2	
Zinc	25-100	20% Total Error at 10% Bias
Nickel	10-50	10% Precision
Chromium	10-100	
Group 2		
Mercury	0.05-2	
Group 3		
Arsenic	10-50	
Group 4 (μg.kg^{-1} dry wt)		
HCB	0.1-2	
PCBs	0.1-2	
Aldrin	0.1-2	50% Total Error at 25% Bias
Endrin	0.1-2	25% Precision
Dieldrin	0.1-2	
p,p'DDT	0.2-5	
p,p'DDE	0.2-5	
p,p'DDD	0.2-5	

Note: For PCBs, analyses will be for specific chlorobiphenyl congeners, to include IUPAC No. 28, 31, 52, 101, 105, 118, 138, 153, 156, 180.

UK MARINE ANALYTICAL QUALITY CONTROL
BIOLOGICAL TISSUE (mg.kg⁻¹ dry wt)

Determinand	Range	Performance Targets
Group 1		
Lead	2-50	
cadmium	0.5-5	
Zinc	10-300	
Group 2		
Mercury	0.1-3	20% Total Error at 10% Bias and 10% Precision
Group 3		
Arsenic	3-20	
Group 4		
Organochlorine Pesticides	5-50	50% Total Error at 25% Bias, 25% Precision
PCBs	5-25	

Note: For organochlorine pesticides, individual compounds should be identified to include dieldrin, α-HCH, γ-HCH, p,p'DDD, p,p'DDE, p,p'DDT, aldrin, endrin, HCB, HCBD.

For PCBs see notes for sediments.

DISTRIBUTION FREQUENCY

Aqueous Samples   Quarterly

Sediment   Quarterly

Biota   Annually

The distribution of the quarterly samples will be fixed so that reports of each distribution will be available for the following NCC meeting.

NOTE ON THE DERIVATION OF ERROR THRESHOLDS FOR MARINE AQC

The report for the first inter-laboratory test carried out under the National Marine AQC programme provided details of the error thresholds used in data interpretation. This note explains the basis for the choice of the thresholds.

An error threshold is maximum allowable difference between the true value for a measured parameter and the measurement itself. It is intended to provide an objective means of identifying analytical results which are in error by more than some agreed, acceptable margin. The size of this margin should be related to the uses of the results, such that errors less than the thresholds are not likely to prejudice the interpretation of the analytical data.

The National Co-ordinating Committee provided WRc with the accuracy target for marine analyses that results should not be in error by more that 20% for metals and nutrients determinations and 50% for trace organics. This percentage target is suitable for most measurements made in the range of interest. However, as concentrations approach zero, a fixed percentage target is both unnecessarily stringent and difficult to achieve. Hence, in deriving error thresholds, it is necessary also to define maximum allowable errors in concentration terms. These absolute targets apply at low concentration and give way to a percentage targets higher in the range of interest.

The thresholds were derived as follows:

1.   The determinand concentrations of interest provided by the NCC were examined. These were listed for low and high level samples. The values for the low samples were taken as a guide to the likely lowest level of interest.

2.   A nominal required Limit of Detection (LOD) was set at one tenth of the lowest level of interest. If laboratories achieve this LOD, the precision of their determinations at the level of interest is likely to be satisfactory.

3.   The error threshold was then defined as equal to the LOD or 20% (50% for organics) of the determinand concentration in the sample, whichever is the larger. This means that, at the concentrations of test samples, a percentage target should usually apply. However, if for some unspiked determinands the concentration is lower than anticipated, the more appropriate (and realistic) absolute target will be used.

NATIONAL MARINE AQC SCHEME - ERROR THRESHOLDS

AQUEOUS SAMPLES

	THRESHOLDS	
Group 1 - Sea Water Nutrients (A and B)	Absolute	%
Ammonia	0.50 μM	20
TON	0.50 μM	20
Nitrite	0.05 μM	20
Orthophosphate	0.05 μM	20
Silicate	0.50 μM	20
Group 2 Estuarine Nutrients (A and B)		
Ammonia	2.0 μM	20
TON	1.50 μM	20
Nitrite	0.20 μM	20
Orthophosphate	0.50 μM	20
Silicate	2.00 μM	20
Group 3 - Trace Metals (A and B)		
Cadmium	0.005 μg/l	20
Copper	0.05 μg/l	20
Lead	0.02 μg/l	20
Nickel	0.05 μg/l	20
Zinc	0.20 μg/l	20
Chromium	0.20 μg/l	20
Group 4 - Mercury (A and B)		
Mercury	0.50 ng/l	20
Group 5 - Organochlorines (A and B)		
α-HCH	0.20 ng/	50
γ-HCH	0.20 ng/l	50
HCB	0.25 ng/l	50
HCBD	0.25 ng/l	50
Group 6 - Chloroform and Carbon Tetrachloride (A and B)		
Chloroform	0.01 μg/l	50
Carbon Tetrachloride	0.01 μg/l	50
Group 7- Pentachlorophenol (A and B)		
PCP	2.50 ng/l	50

SEDIMENTS

	THRESHOLDS	
Group 1	Absolute	%
Copper	1.00 mg/kg	20
Lead	2.00 mg/kg	20
Cadmium	0.05 mg/kg	20
Zinc	2.50 mg/kg	20
Nickel	1.00 mg/kg	20
Chromium	1.00 mg/kg	20
Mercury	0.005 mg/kg	20
Arsenic	1.00 mg/kg	20
Group 2		
HCB	0.01 μg/kg	50
PCBs	0.01 μg/kg	50
Aldrin	0.01 μg/kg	50
Endrin	0.01 μg/kg	50
Dieldrin	0.01 μg/kg	50
p,p-DDT	0.02 μg/kg	50
p,p-DDE	0.02 μg/kg	50
p,p-DDD	0.02 μg/kg	50

BIOTA

	THRESHOLDS	
Group 1	Absolute	%
Lead	0.20 mg/kg	20
Cadmium	0.05 mg/kg	20
Zinc	1.00 mg/kg	20
Mercury	0.01 mg/kg	20
Arsenic	0.30 mg/kg	20
Group 2		
Organochlorine Pesticides	0.50 μg/kg	50
PCBs	0.50 μg/kg	50

PARTICIPATING LABORATORIES IN THE NATIONAL MARINE

AOC SCHEME - YEAR ONE

British Geological Survey

Clyde River Purification Board

Dept of Agriculture Northern Ireland Aquatic Sciences

Dept of Agriculture Northern Ireland, Food and Agriculture

Highland River Purification Board.

Industrial Research and Technology Unit

Ministry of Agriculture, Fisheries and Food, Burnham-on-Crouch

Ministry of Agriculture, Fisheries and Food, Lowestoft

NRA	Anglian
NRA	Northumbria
NRA	North West, Carlisle
NRA	North West, Warrington
NRA	Severn Trent
NRA	Thames
NRA	South West
NRA	Welsh, Llanelli
NRA	Yorkshire

Scottish Office, Agriculture and Fisheries Department

Solway River Purification Board

Tay River Purification Board

NOTE: The University of East Anglia participated as a substitute for MAFF (Lowestoft) in distribution 2.

Return to: Dr A Griffiths, Forth River Purification Board, Heriot-Watt Research Park, Avenue North, Riccarton, Edinburgh, EH14 4AP by 23 June 1992.

Determinand Group	Laboratory Name	
	1.	2.
Aqueous		
1		
2		
3		
4		
5		
6		
7		
8		
Sediment		
1		
2		
3		
4		
Biological		
1		
2		
3		
4		

Laboratory Address 1. .... 2. ....

....

....

Name of Contact 1. .... 2. ....

Samples for the third inter-laboratory test were distributed on 17 February 1993. The test comprised:-

AQUEOUS SAMPLES

GROUP 1) (Ammonia, TON, Nitrite, Orthophosphate and Silicate in Seawater)

Sample A   Two litres of filtered, unpreserved, sterilised seawater and one mixed spiking solution for ammonia and nitrite.

Sample B   Two litres of filtered, unpreserved, sterilised seawater and one mixed spiking solutions for ammonia, nitrite and orthophosphate, and one spiking solution for TON).

GROUP 2) (Ammonia, TON, Nitrite, Orthophosphate and Silicate in Estuarine Water)

Sample A   Two litres of filtered, unpreserved, sterilised estuarine sample (of salinity approximately 5%) and a mixed spiking solution for ammonia and nitrite.

Sample B   Two litres of filtered, unpreserved, sterilised estuarine sample (of salinity approximately 5%) and one mixed spiking solution for ammonia, nitrite and orthophosphate and one spiking solution for TON.

GROUP 3) (Cadmium, copper, lead, nickel, zinc and chromium)

One litre of filtered seawater sample for Sample A and one litre for Sample B (each preserved with 0.2% nitric acid)

GROUP 4) (Total Mercury) One litre of filtered seawater sample for Sample A and one litre for Sample B (each preserved with 0.6% nitric acid).

GROUP 5) (αHCH, γHCH, HCB and HCBD) Two litres of filtered, unpreserved seawater and a spiking solution for Sample A and two litres of seawater and a spiking solution for Sample B.

GROUP 6) (Chloroform and carbon tetrachloride) Two litres of filtered, unpreserved seawater and a spiking solution for Sample A and two litres of seawater and a spiking solution for Sample B.

GROUP 7) (Pentachlorophenol) Two litres of filtered, unpreserved seawater and a spiking solution for Sample A and two litres of seawater and a spiking solution for Sample B.

MARINE SEDIMENTS

GROUP 1)   (Copper, Lead, Cadmium, Zinc, Nickel, Chromium, Mercury and Arsenic)

25 g of a dried, sieved (63 μm) marine sediment.

GROUP 2)   (HCB, PCBs, Aldrin, Endrin, Dieldrin, p,p-DDT, p,p-DDE and p,p-DDD)

Two portions of a dried, sieved (63 μm) marine sediment. Weight as specified by the laboratory for a routine determination.

BIOTA

GROUP 1   (Lead, Cadmium, Zinc, Mercury and Arsenic)

4g of a freeze dried, sieved (250 μm) fish tissue.

GROUP 2   (Dieldrin, α-HCH, γ-HCH, p,p-DDD, p,p-DDT, Aldrin, Endrin, HCB, HCBD, and PCB's). 5g of fish oil.

Distribution number   : 01
Date set   : Aqueous determinands
Date of distribution   : 2 September 1992

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Laboratory number

Determinand	4	7	7	16	17	3	14	18	10	2	1	15	21	12	11	19	5
Group 1 - Seawater sample A																	
- Ammonia (A)	-20	-10		-13			-4	-27f	29f		26f		41f		3			-13
* TON (A)	1364f			9999f				63		-60							-2	
~ Nitrite (A)	-2	-1		-7			-7	31f	-10	-4		1		1				-11
~ Orthophosphate (A)	-4	16		-10			-2	-12	1	-5		43f		2			2	-10
* Silicate (A)	-8	-6		6			-9	21	12	-15		-8		1			-54f	5
Group 1 - Seawater sample B																	
- Ammonia (B)	49f	-17		-25f			-4	-27f	4		4		15		-1			-19
- TON (B)	-59f	-31f					6	7	1	14		-2		0			-1	-3
~ Nitrite (B)	5	4		-8			-3	8	-3	-4		-3		-1				0
- Orthophosphate (B)	-19	14		-7			-2	3	-2	31f		-5		-2			-3	-3
* Silicate (B)	2	-3		1			8	-3	21f		-8		-9		2		-15	4
Group 2 - Estuarine sample A																	
~ Ammonia (A)	60f	-75f					12		0		10		-2	-5	3			2
* TON (A)	-5	-26f					-4		5		-11		0	5	6		2	2
~ Nitrite (A)	-5	387f					-5		-3		-8		-6		-8			-2
- Orthophosphate (A)	-12	11					-1		-6		-28f		-4	-11	-2		-5	-1
* Silicate (A)	-1	1					2		4		-4		-8	-3	3		2	5
Group 2 - Estuarine sample B																	
~ Ammonia (B)	25f	-82f					3		2		9	-20f	5	4	4			5
- TON (B)	-94f	-46f					-7		-1	124f	-13		-6	2	-1		-5	-5
~ Nitrite (B)	0	403f					4		3	-18	60f	-1			-2			6
- Orthophosphate (B)	-5	17					1		-2		-34f	5	0	1	2		-1	0
- Silicate (B)	-1	2					4		2		-3		-5	-3	0		1	3
Group 3 - Trace metals sample A																	
* Dissolved Cadmium (A)	-48f	33f		11	-11								10	36f		-31f	
- Dissolved Copper (A)	-4	4		229f	8							-24f	179f	-17		-32f	
~ Dissolved Lead (A)	174f	41f		-33f	14				-59f					-18		11	
* Dissolved Nickel (A)	-52f	19		-3	14				165f			5		26f		-10	
* Dissolved Zinc (A)	-23f	-25f		43f	-13				53f			-22f				-13	
- Dissolved Chromium (A)	4			-90f					-30f					-22f			
Group 3 - Trace metals sample B																	
- Dissolved Cadmium (B)	-25f	3		-23f	-31f				-16				-21f	10		-12	
~ Dissolved Copper (B)	11	-35f		-4	9				33f			-10	45f	-13		-2	
- Dissolved Lead (B)	42f	-21f		-11	10				-35f			2	-15	-6		0	
- Dissolved Nickel (B)	-28f	-7		-2	12				68f			0		4		0	
- Dissolved Zinc (B)	-13	13		21f	6				-8			-4	-44f	3		8	
- Dissolved Chromium (B)	-14			-91f					-53f					-20f			
Group 4 - Mercury sample A																	
- Total Mercury (A)	13	-21f						-41f									
Group 4 - Mercury sample B																	
- Total Mercury (B)	52f	13		-37f										-5			
Group 5 - Organochlorines sample A																	
~ a-BCH (A)				-49		-33f		-55f	-43			458f		22	14	27	0
* g-BCH (A)				-10	-10	-47		-64f	-41		12	49	55f	53f	10	-6	
- BCB (A)				24	34			-16	-22			44	34	-9	7	7	
~ BCBD (A)				91f	15				-42			57f		-4	19		
Group 5 - Organochlorines sample B																	
- a-BCH (B)				-59f		-45		-70f	-28			119f	20	-1	-18	13	-6
~ g-BCH (B)				-23	-16	-38		-30	-23		23	38	28	61f	-10	-4	
~ BCB (B)				-19	44			18	-19			20	37	-1	-14	-17	
- BCBD (B)				-63f	-36f				-17			31		-20	-14		
Group 6 - Chloroform and Carbontetrachloride sample A																	
- Chloroform (A)								48	36		-20	56f		8	36f		
- Carbon Tetrachloride (A)								36	1		46	-6		36	-49	9	
Group 6 - Chloroform and Carbontetrachloride sample B																	
- Chloroform (B)								27	-1		-23	-2	-9	19	0	19	
- Carbon Tetrachloride (B)								39	-2		-21	-21	19	51f	-27	2	
Group 7 - Pentachlorophenol sample A																	
* PCP (A)				46					-3			-11	-60f	32	-12		7
Group 7 - Pentachlorophenol sample B																	
* PCP (B)				27					-21			-4	-61f	35	-5		29

Notes: f indicates failure to achieve the present standard of accuracy
* Mean of all laboratories used for calculating mean difference
~ Nominal value used for calculating mean difference
9999 indicates a value u 9999; -999 indicates a value u -999

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 01
Data set   : Sediment determinands
Date of distribution : 2 September 1992

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Determinand	4	17	3	14	18	10	9	15	21	12	11	19	8	23
Group 1														
- Copper	63f	-10	-10	16	11	66f	2		-17	7	17	-16	0	
~ Lead	-61f	-6	-28f	62f	-67f	-14	9		-8	15	4	-19	-16	
* Cadmium	4	-20f		1003f	73f	411f				10	14		-80f	
* Zinc	2	0	-15	15	20	-12	-6		-7	16	-8	-3	48f	
* Nickel	5	-6	-8	43f	55f	-14	-21f		-17	-12	15	-20f	-19	
* Chromium	40f	22f	-14	18	16	-24f	-7		-44f	-1	29f	-14	-21f	
*• Mercury	24f	-19	-26f	-19	58f	-35f	15		-18	-6	15	9	1	
* Arsenic	-56f			45f	16		23f			-5	-22f			
Group 2														
~ HCB				-46	-24	9	225f	72f		-20	243f	-39		
~ PCB 28				-55f	-10	17				73f		-23		
* PCB 31				-97f	4	-4								
~ PCB 52				-65f	-5	-43	325f			1		-26		
~ PCB 101				-52f	13	50f				120f	80f	0		220f
* PCB 105				-78f	46	32								
~ PCB 118				-27	90f	88f	163f			275f	375f	21		1225f
* PCB 138				-68f	-9	-6	64f			27	22	-30		492f
? PCB 153				-68f	7	-3	35			24	19	-15		614f
* PCB 156				-39	2	36								
~ PCB 180				-52f	14	-3	26			93f	82f	12		707f
~ Aldrin						-71f	-86f				18			-4
~ Endrin					-27	32					39			115f
~ Dieldrin				-55f	-16	-27	900f				15			-37
* pp'DDT				-58f	-52f	-35	2834f				73f			73f
~ pp'DDE				-32	0	22		52f		17	9	-30		3
~ pp'DDD				-58f	-23	-4		3		-29	9	-25		35

Notes:
f indicates failure to achieve the preset standard of accuracy
* Mean of all laboratories used for calculating mean difference
- Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 02
Data set   : Aqueous determinands
Date of distribution : 15/01/93

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Determinand	1	2	3	4	5	7	10	11	12	13	14	15	16	17	18	19	21
Group 1 – Seawater sample A																	
Ammonia (A)		-30f		-24f	-4	27f		-19	-7	-15	16	-22f			4		
TON (A)		6		3	-13	40f			-5	-6	16	-38f			-1	-3	
Nitrite (A)		6		4	1	-1		-4	1216f	5	-3	-10			-4	17	
Orthophosphate (A)		-9		4	5	-6		12	-11	16	-10	:			-4	3	
Silicate (A)				-1	3	-9		1	-54f	-2	-19	:			6	3	
Group 1 – Seawater sample B																	
Ammonia (B)		-3		-1	-3	-72f		-5	-16	8	15	-::			4		
TON (B)		17		7	-4	6			-6	-11	2	-44f			-2	-9	
Nitrite (B)		7		6	4	21f		-1	180f	8	-3	-::			0	7	
Orthophosphate (B)		3		5	11	2		7	-3	-8	-12	-:			0	0	
Silicate (B)				7	19	-8		2	-54f	-8	-18	-:			8	0	
Group 2 – Estuarine sample A																	
Ammonia (A)		-5		-4	23f	48f		6	-23f		5				11		4
TON (A)		23f		21f	0	40f		6			22f				4	-1	
Nitrite (A)		12		9	5	9		1	128f		-2				1		
Orthophosphate (A)		3		1	1	4		3	0		-12				-27f	-3	
Silicate (A)		10		13	15	3		8	-25f		-5				0	5	-23f
Group 2 – Estuarine sample B																	
Ammonia (B)	-21f	63f		-2	3	45f		-4	-5		8				7		2
TON (B)	-90f	10		8	-1	-17		5			-2				-1	1	
Nitrite (B)	-1	7		4	3	-1		0	30f		-3				0		
Orthophosphate (B)	-30f	-23f		2	-1	4		5	5		-8				-17	-1	-2
Silicate (B)	2	4		4	0	-9		1	-28f		-7				-2	2	4
Group 3 – Trace metals sample A																	
Dissolved Cadmium (A)	57f		-6	-2		16	-19	8			2			-22f		7	15
Dissolved Copper (A)	37f		-7	4		4	92f	-9			0			4		14	-9
Dissolved Lead (A)	644f		6	29f		13	-48f	-14						-36f		-36f	-24f
Dissolved Nickel (A)	21f		-20f	14		14	-19	-7			-3			-9		9	
Dissolved Zinc (A)	56f		-3	2		-28f	37f	-37f			-90f			-34f		7	
Dissolved Chromium (A)	34f			-16				5									
Group 3 – Trace metals sample B																	
Dissolved Cadmium (B)	17		-5	-13		-4	-23f	9			0			-27f		-2	7
Dissolved Copper (B)	10		-6	-4		7	40f	2			1			-6		7	7
Dissolved Lead (B)	2		-8	-1		-16	-34f	-6			-6			12		-4	-14
Dissolved Nickel (B)	-9		-23f	-2		-8	-7	-8			-4			-11		4	
Dissolved Zinc (B)	14		10	-12		-13	14	8			-89f			-3		0	
Dissolved Chromium (B)	-11			-9			-57f	2									
Group 4 – Mercury sample A																	
Total Mercury (A)	6			21f													
Group 4 – Mercury sample B																	
Total Mercury (B)	1			56f		-9		1			10	-38f					8
Group 5 – Organochlorines sample A																	
a-HCB (A)	858f			-14		-15	83f	52f			-41	-54f			13	-2	81f
g-BCB (A)	-16			34		-6	58f	4			-21	-46			13	10	44
HCB (A)				10		-15	132f	26			-41	-54f	-66f		-11	26	152f
HCBD (A)				127f		85f	6	8			-42				-1		258f
Group 5 – Organochlorines sample B																	
a-HCH (B)	278f			21		-1	45	16			-36	-51f			6	-4	22
g-HCH (B)	-29			104f		5	5	16			-26	-46			-1	3	19
HCB (B)				46		-14	26	-11			-48	-61f	-98f		-22	-16	-3
HCBD (B)				-27		3	-8	1				-51f			-2		105f
Group 6 – Chloroform and Carbontetrachloride sample A																	
Chloroform (A)								93f	6		11				28		
Carbon Tetrachloride (A)								-21	3		20				-7	-10	
Group 6 – Chloroform and Carbontetrachloride sample B																	
Chloroform (B)	37							-4	7		13				12	32	12
Carbon Tetrachloride (B)	-27							-28	31		6				-4	7	43
Group 7 – Pentachlorophenol sample A																	
PCP (A)				18		7	53f	4			23			110f	31	121f	
Group 7 – Pentachlorophenol sample B																	
PCP (B)	0			-8		-12	-11	-16			-3			7	-16	62f	-31

Note: f indicates failure to achieve the present standard of accuracy
       ° Mean of all laboratories used for calculating mean difference
       ~ Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 02
Data set : Sediment determinands
Date of distribution : 18/01/93

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Determinand	1	3	4	6	7	8	9	10	11	12	14	15	17	18	19	21
Group 1																
• Copper	-13	-1	20f	-5	-16	-4	-9	1	17	17	-100f		-3	4	-5	-3
• Lead	10	-6	5	-8	-5	0	-8	1	12	14	-14		-7	-23f	29f	1
• Cadmium	-4		-13		16			-10	-4	16			-100f	575f		
• Zinc	-1	1	-11	-2	-10	17	2	-22f	12	21f	-26f		3	9	5	2
• Nickel	-6	-8	14	16	-12	4	-5	7	66f	8			2	-11	-2	-7
• Chromium		1	53f	-12	-27f	-23f	-29f	-7	24f	6			39f	0	-4	-21f
Group 2																
• Mercury		-17	19		-11	-23f	6	233f	12	21f	-55f			44f	8	-4
Group 3																
• Arsenic			-6				9		-8	6						
Group 4																
~ HCB		-54f				-61f			-44	-88f	-53f	467f		-17	-42	
• PCB 28		-8							-5	226f	-16	1100f		21	8	
• PCB 31		-17									1			16		
• PCB 52		-61f							110f		5			1	-55f	
• PCB 101		-72f								37	-67f	157f		3	-58f	
~ PCB 105		-12									35			76f		
• PCB 118		-15							34	170f	-16	940f		-5	2	
• PCB 138		-14							-42	59f	-17	550f		-17	30	
• PCB 153		-74f							-74f	-43	157f	144f		-64f	-46	
~ PCB 156		2									6			97f		
• PCB 180		-33								30	-48	374f		-42	92f	
~ Aldrin						-70f			-78f			247f		-67f		
~ Endrin						1			-35		-21	88f		-24		
~ Dieldrin						-39			-18		0	287f		-33		
• pp'DDT		-9				490f			-31		-1	42		-15	14	
~ pp'DDE		-9				-52f			-4	-68f	-5	411f		44	-16	
~ pp'DDD		-10				-19			-34	-95f	-23	70f		7	-16	

Notes:
f indicates failure to achieve the preset standard of accuracy
• Mean of all laboratories used for calculating mean difference
~ Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 03
Data set : Aqueous determinands
Date of distribution : February 1993

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Laboratory number

Determinand	1	2	3	4	5	7	10	11	12	13	14	15	16	17	18	19	21
Group 1 - Seawater sample A																	
- Ammonia (A)		15		-27f	51f	-5		670f	14	0	3	32f	-37f		39f		
* TON (A)		11		-14	-10	-12		-8	2	4	8	3	-39f		14	1	
- Nitrite (A)		-3		4	19	5			-27f		-22f	8	-3			10	
* Orthophosphate (A)		-10		-30f	10	-4		0	7	-6	5	2	120f		-1	-3	
* Silicate (A)		75f		-6	-8	-43f			-2	2	3	-2	2		11	0	
Group 1 - Seawater sample B																	
- Ammonia (B)		5		-20f	32f	4		-25f	-8	4	7	15	-22f		8		
- TON (B)		6		5	25f	-19		14	-3	-2	-39f	1	-42f		1	7	
- Nitrite (B)		-2		9	4	0		-63f	6		-5	-3	1		-5	2	
- Orthophosphate (B)		-1		0	19	-1		-30f	20	-2	-7	-10	3		1	4	
* Silicate (B)		69f		17	-13	-26f			2	6	11	-7	0		11	0	
Group 2 - Estuarine sample A																	
- Ammonia (A)		-7		-9	23f	19		-7	1	3		8			5		-12
* TON (A)		2		1	-2	-31f		4	0	0		0			4	-5	-5
- Nitrite (A)		-7		9	-2	-1			-4			4			8	9	
* Orthophosphate (A)		1		1	3	5			11	3		-9			-16	0	
* Silicate (A)		89f		2	6	-10			4	1		-3			-1	4	-3
Group 2 - Estuarine sample B																	
- Ammonia (B)		-1		-5	4	21f		17	0	3		9			3		0
* TON (B)		-2		1	-1	-43f		6	-4	-2		1			1	-3	3
- Nitrite (B)		-5		5	1	-1		-37f	-6			-1			2	6	
- Orthophosphate (B)		3		3	-1	2		-9	7	-1		-3			-9	3	5
* Silicate (B)		67f		3	2	-9			3	4		-1			0	2	-5
Group 3 - Trace metals sample A																	
- Dissolved Cadmium (A)			-12	71f		6	-6			1					10			-2
* Dissolved Copper (A)			-17	5		-9	44f			-4			-2		-6	-63f		51f
- Dissolved Lead (A)			2	13		-26f				-2					44f	-28f		-19
* Dissolved Nickel (A)			5	8		-20	62f			-7			4		10			
* Dissolved Zinc (A)	182f		11	-13		-38f	26f			-2					9	-11	16	
- Dissolved Chromium (A)	23f			-23f			-50f			-3						-44f		
Group 3 - Trace metals sample B																	
- Dissolved Cadmium (B)			-24f	8		0	-10			-5			-10		-11	-63f		4
- Dissolved Copper (B)			-14	9		-5	10			2			-2		-11	4	-39f	11
- Dissolved Lead (B)			-18	9		-63f	-20f			1			-7		-3	-7	-56f	1
- Dissolved Nickel (B)			-3	1		-26f	20f			-3			-5		-10	-74f		
- Dissolved Zinc (B)	53f		-9	-32f		-10	3			-2					-4	0	6	
- Dissolved Chromium (B)	6			-13			-56f			3						1		
Group 4 - Mercury sample A																	
- Total Mercury (A)				26f		-34f			-23f								
Group 4 - Mercury sample B																	
- Total Mercury (B)				65f		-29f			-15			38f					
Group 5 - Organochlorines sample A																	
- a-BCH (A)				-44		28		-24	4		-10	63f		39	26	28	25
- g-BCH (A)				17		19		-58f	-32		38	39	233f	-14	20	43	72f
- BCB (A)				31		-24		-23	7			-9		92f	-29	15	-29
- BCBD (A)				17		149f			-53f			72f	110f	30	-1		207f
Group 5 - Organochlorines sample B																	
- a-BCH (B)				10		-12		-6	48		-3	30		13	-12	1	10
- g-BCH (B)				75f		-2		-11	-6		14	10	-67f	-37	-15	10	33
- BCB (B)				59f		-15		-7	6			21	-4	-11	-21	-2	-22
- BCBD (B)				-40		17		11	-44			12	129f	3	-26		-30
Group 6 - Chloroform and Carbontetrachloride sample A																	
- Chloroform (A)	-12						15	27	2			-5			22		
- Carbon Tetrachloride (A)	22						-17	6	19			11			-22	11	
Group 6 - Chloroform and Carbontetrachloride sample B																	
- Chloroform (B)	38						1	4	15			-12			-8	6	-8
- Carbon Tetrachloride (B)	-7						-22	-4	32			12			-26	9	48
Group 7 - Pentachlorophenol sample A																	
- PCP (A)				64f		-9	-1	68f	45			-20			6		
Group 7 - Pentachlorophenol sample B																	
- PCP (B)				37		-9	-73f	22	4						-3		

Notes:
f indicates failure to achieve the preset standard of accuracy
* Mean of all laboratories used for calculating mean difference
- Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 03
Data set : Sediment determinands
Date of distribution : February 1993

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Determinand	1	3	4	6	7	8	9	10	11	12	14	15	17	18	19	21
Group 1																
• Copper	-5	-2	9	6	-13	-2	-1	10	7	20	-5		-6	2	-17	-1
• Lead	-3	-4	-2	-4	24f	-10	-7	-3	2	9	21f		-19	5	-15	6
• Cadmium	-14		34f		-2			-9	8	24f	-62f		21f	187f		
• Zinc	-4	-10	1	-2	7	-6	13	8	-5	15	0		-8	-2	-12	4
• Nickel	-17	-2	1	16	3	-1	3	4	13	9			-3	53f	-13	-13
• Chromium	-54f	9	36f	-2	-26f	-7	-1	-1	45f	11			36f	-22f	0	-25f
• Mercury	-16	-17	23f	-14	11	-14	11	25f	-4	-8	-57f			1	5	-3
• Arsenic			-43f				-8		-6	20f				38f		
Group 2																
• HCB		-11	-64f			8				0				47	-30	51f
~ PCB 28		-15												35	-24	0
~ PCB 31		-13												27		
~ PCB 52		-18	-40							104f				59f	-26	55f
~ PCB 101		-25	-48			10				41				11	-16	-10
~ PCB 105		-55f	-41			45				12				76f		-5
~ PCB 118		-15	-41			121f				14				-15	-25	-19
~ PCB 138		-22	-40							37				4	-18	
~ PCB 153		-12				27				22				12	-8	
~ PCB 156		-29	-32							92f				-1	-12	0
~ PCB 180		-11	-37							24				-23	-2	
~ Aldrin										-86f				-79f	-74f	
~ Endrin			-73f			170f					-29			-25	-13	
~ Dieldrin		97f	-22							68f	20			3		45
~ pp'DDT		49	-90f			7					-21			-21	1	-13
~ pp'DDE		-16	-45			30				-52f				-11	-18	-2
• pp'DDD		49								34	-61f			-22		

Notes:
f indicates failure to achieve the preset standard of accuracy
• Mean of all laboratories used for calculating mean difference
~ Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 03
Data set : Marine Biota
Date of distribution : February 1993

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Determinand	Laboratory number											
	1	3	4	7	8	9	11	12	14	16	18	21
Group 1												
* Lead			-43				7	87	760f	3235f		-51
* Cadmium			-35				-31		-5	3049f	9999f	72
* Zinc	2	-21f	6	-3	4	8	0	21f	4	75f	-21f	
* Mercury	42f		46f	44f	9	15	14	15	-39f	4900f	-62f	-83f
* Arsenic						62		36			-99	
Group 2												
~ Dieldrin		7			62f			204f	-10		14	-17
~ a-HCH		9			7			14	-55f		-23	12
~ g-HCH		-58f			132f				-47		-36	16
* PP 'DDD		9			-28			-28	9		27	10
~ PP 'DDE		15			77f			-52f			75f	15
~ PP 'DDT		48			81f			-3	0		50f	-17
~ Aldrin					-36			-22			-27	-19
~ Endrin					395f			0	-20		117f	-15
~ HCB		-26			-18			-16			10	-14
~ HCBD					-49			11			2	-5
~ PCB (28)		8									6	
~ PCB (31)		-6									14	
~ PCB (52)		-17						-33			32	
~ PCB (101)		-17			14			-63f			2	-16
~ PCB (105)		-39			41			-68f			10	-10
~ PCB (118)		2			56f			-73f			-5	23
~ PCB (138)		4			-11			-61f			20	-6
~ PCB (153)		-1			21			-70f			24	-14
~ PCB (156)		-3			49			-79f			6	-17
~ PCB (180)		-9			122f			-68f			-29	

Notes:
f indicates failure to achieve the preset standard of accuracy
* Mean of all laboratories used for calculating mean difference
~ Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 04
Data set : Aqueous determinands
Date of distribution : MAY 1993

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Laboratory number

Determinand	1	2	4	5	7	10	11	12	13	14	15	16	17	18	19	20	21
Group 1 - Seawater sample A																	
- Ammonia (A)		-13	6	43f	42f		90f	-20	-20	-15	-9	-31f		36f	-17	-30f	
* TON (A)			66	-23	31			-38	-52	122		-52		13	-65		
~ Nitrite (A)		20	15	4	8			-16		62f	10	0		3	6	27f	
~ Orthophosphate (A)		-10	-1	-16	8		-41f	6	-10	8	13	1		-12	-8	-6	
* Silicate (A)		-62	20	29	-54			-15	8		81			-8			
Group 1 - Seawater sample B																	
- Ammonia (B)		12	10	149f	37f		43f	22f	2	-14	22f	-6		29f	6	-3	
* TON (B)		4	17	0	-9			-14	-1	0	1	-33f		-2	7	-2	
~ Nitrite (B)		10	12	3	2			-6		51f	0	2		-2	21f	18	
- Orthophosphate (B)		-2	-1	6	22f		-14	24f	-3	-34f	0	1		-1	-5	10	
* Silicate (B)		14	4	5	-14			-3	6	12	-6	-24f		9	-4	1	
Group 2 - Estuarine sample A																	
- Ammonia (A)		-30f	5	-9	49f		22f	1	0		9		-5	6	31f	-8	34f
* TON (A)		2	-56f	0	-28f			-1	0		1			5	-3	-3	0
~ Nitrite (A)		7	8	-3	2			2			0		-17	0	4	10	
* Orthophosphate (A)		0	8	-1	27f		-17	14	-2		-5		1	-17	-5	-9	1
* Silicate (A)		8	3	-2	-9			3	-2		-2			3	-2	0	22f
Group 2 - Estuarine sample B																	
- Ammonia (B)	-5	2	9	-9	31f		-4	2	1		3			0	3	-7	8
* TON (B)	-6	2	5	0	-34f			4	-1		0			3	-2	-5	-1
- Nitrite (B)	-6	3	3	1	-2			2			-2		-1	0	1	18	
- Orthophosphate (B)	-12	3	7	2	27f		-9	10	-1		0		-17	-3	0	-2	2
- Silicate (B)	-1	4	-1	-4	-15			-4	-4		-5			-1	-1	-2	21f
Group 3 - Trace metals sample A																	
- Dissolved Cadmium (A)			0		26f	-35f		-18					-2		-21f		-18
- Dissolved Copper (A)			-1		30f	148f		51f			0		-27f	0	-1		199f
~ Dissolved Lead (A)			14			-49f		-20f					23f				
* Dissolved Nickel (A)			1		68f	166f		-10			5		-16	18	2		
* Dissolved Zinc (A)	26f		-21f		-29f	61f		-8			-20f		2	-3	-9		
- Dissolved Chromium (A)	6		-33f			-5		-4						-19			
Group 3 - Trace metals sample B																	
- Dissolved Cadmium (B)			-31f		10	-34f		-9			-4		-23f	-45f	-1		-9
~ Dissolved Copper (B)			15		15	48f		5			-1		-21f	-22f	0		54f
- Dissolved Lead (B)			-15		5	-37f		-5			-7		-1	-19	-2		-4
- Dissolved Nickel (B)			12		10	65f		0			16		-16	-15	-6		▶
~ Dissolved Zinc (B)	-1		-5		-11	24f		-3			-13		-5	-1	-2		
- Dissolved Chromium (B)	24f		-18			-37f		1						-21f			
Group 4 - Mercury sample A																	
- Total Mercury (A)	-4		60f		1			17					-17				57f
Group 4 - Mercury sample B																	
- Total Mercury (B)	-23f		16		0			-2					-36f				-30f
Group 5 - Organochlorines sample A																	
- a-BCB (A)			70f		148f			44			28		-4	-2	-2		12
- g-BCB (A)			23		100f						4	-23	-11	-18	8		1
- BCB (A)			53f				-27	28			15	77f	-20	24	7		54f
- HCBD (A)			-3		10		88f	-10			35	167f	5	-39			41
Group 5 - Organochlorines sample B																	
- a-BCB (B)			18		76f		-11	-43			20		64f	-14	-4		9
- g-BCB (B)		-36	-3		36		-20	-13			-6	-5	-34	-16	6		2
- BCB (B)			79f		-22		-16	0			-4	16	50	-11	0		16
~ HCBD (B)			-35		8		-10	-31			13	17	17	-40			9
Group 6 - Chloroform and Carbontetrachloride sample A																	
- Chloroform (A)		28					15	8	20		1			17			
- Carbon Tetrachloride (A)		-12					1	-13	26		11			-3	-21		
Group 6 - Chloroform and Carbontetrachloride sample B																	
- Chloroform (B)		-1					7	-6	19		11			-10	56f		
- Carbon Tetrachloride (B)		-18					1	-21	35		2			-33	16		
Group 7 - Pentachlorophenol sample A																	
- PCP (A)			43		-13	45	0	8			-11		69f	12			54f
Group 7 - Pentachlorophenol sample B																	
~ PCP (B)		-87f	22		-25	16	-15	2			41		56f	-14	-9		23

Notes:
f indicates failure to achieve the preset standard of accuracy
* Mean of all laboratories used for calculating mean difference
~ Nominal value used for calculating mean difference

SUMMARY OF LABORATORIES' RESULTS

Distribution number : 04
Data set   : Sediment determinands
Date of distribution : MAY 1993

MEAN DIFFERENCES FROM REFERENCE CONCENTRATION (%)

Determinand	Laboratory number 1	3	4	6	7	8	9	10	11	12	15	17	18	19
Group 1														
* Copper	-11	-2	14	-11	-11	0	-5	-9	-7	30f		3	15	-6
* Lead	-6	4	10	3	2	-1	23f	-7	1	14		-6	-23f	-15
~ Cadmium			7	-11	21			2	800f	0		-17	724f	
* Zinc	-15	1	2	-2	1	7	6	-14	-1	11		1	3	1
* Nickel	-32f	-9	-3	10	-9	0	27f	-7	8	23f		2	6	-15
*. Chromium	-39f	-4	18	-13	-27f	43f	-12	-26f	42f	-1		31f	3	-17
* Mercury	1	44f	228f	-37f	-11	-19	11		-14	-6			61f	-30f
* Arsenic	-14						4		-8	16			2	
Group 2														
~ HCB							-69f			87f	-15		6	-12
~ PCB 28											26		84f	53f
~ PCB 31											23		49	
~ PCB 52						300f	200f			1900f	-1		12	-8
~ PCB 101							453f			460f	-26		-5	-3
~ PCB 105							7				-2		2	13
~ PCB 118							8			114f	0		19	38
~ PCB 138						-36	-53f			58f	-1		-15	-7
~ PCB 153						14	-45			23	-4		16	2
~ PCB 156						51f	-61f				-17		-13	0
~ PCB 180						53f	-42			94f	-13		-36	19
~ Aldrin						-18	-59f				-43		-60f	-60f
~ Endrin											31		-9	-11
~ Dieldrin							13				-10		-13	38
~ pp'DDT						29	38				-36		-27	20
~ pp'DDE						40	-29			151f	-12		11	-1
~ pp'DDD						7	32				-16		31	46

Notes:
f indicates failure to achieve the preset standard of accuracy
* Mean of all laboratories used for calculating mean difference
~ Nominal value used for calculating mean difference

Aqueous Nutrients
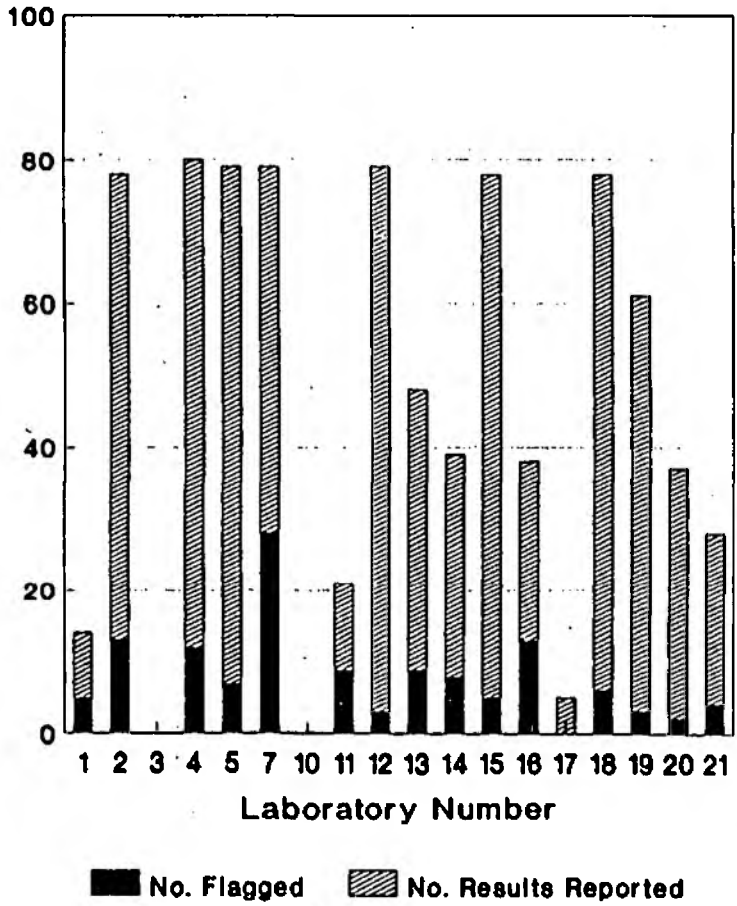
Laboratory Number

No. Flagged   No. Results Reported

Aqueous Metals

Laboratory Number

No. Flagged   No. Results Reported

Aqueous Organics

Laboratory Number

No. Flagged   No. Results Reported

Sediment Metals

Laboratory Number
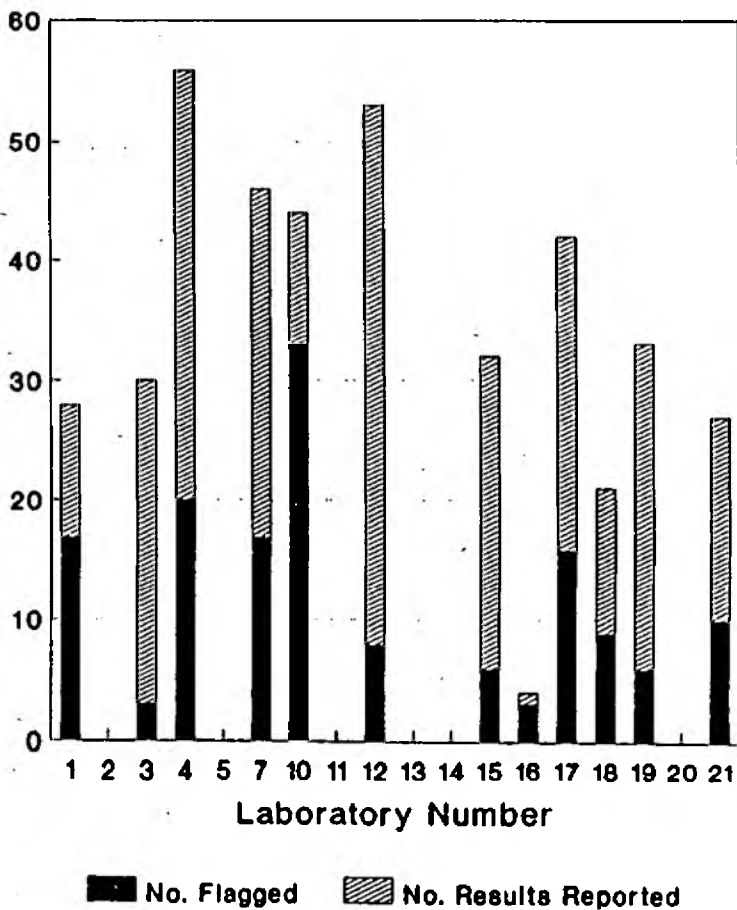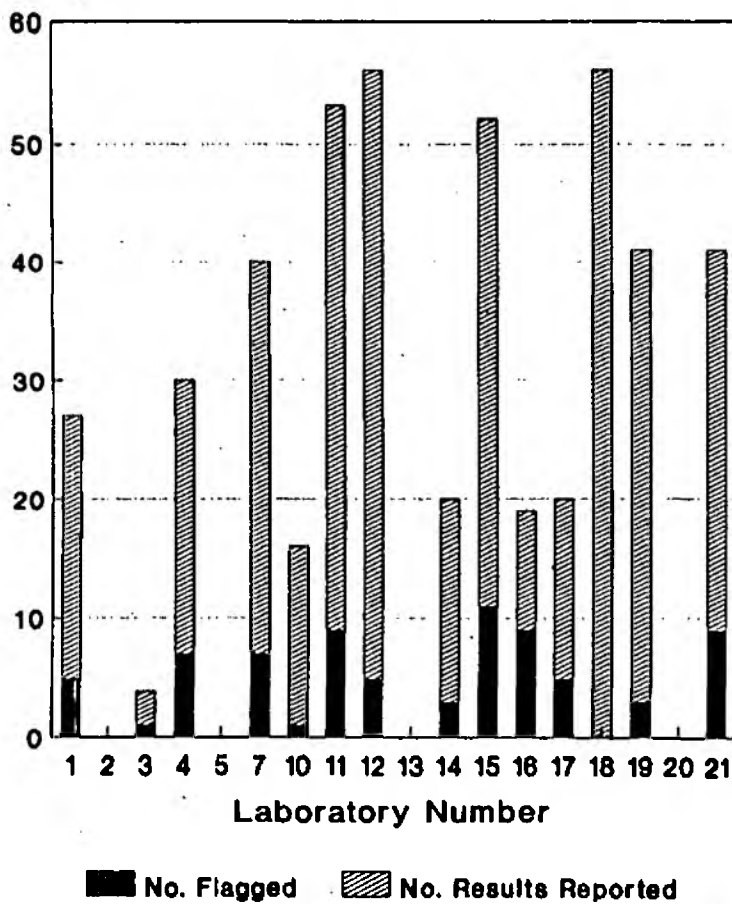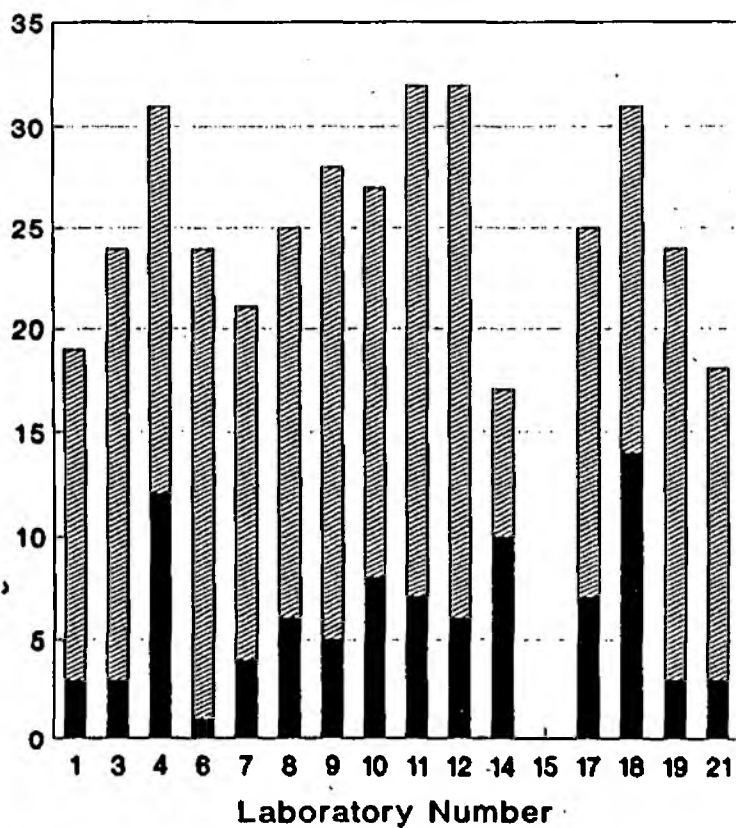
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Sediment Organics

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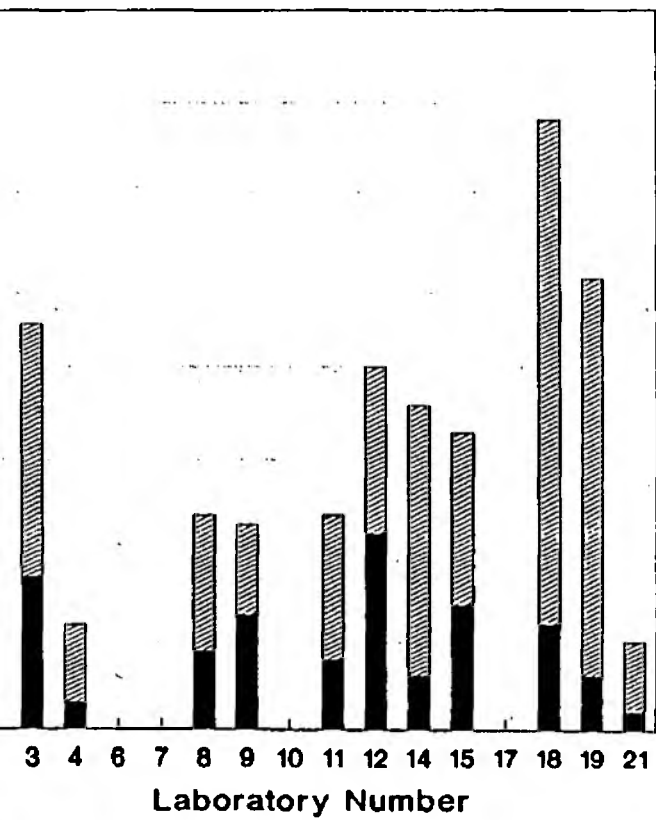
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Biota Metals

Laboratory Number

No. Flagged ▓ No. Results Reported

Biota Organics

Laboratory Number

█ No. Flagged   ▨ No. Results Reported
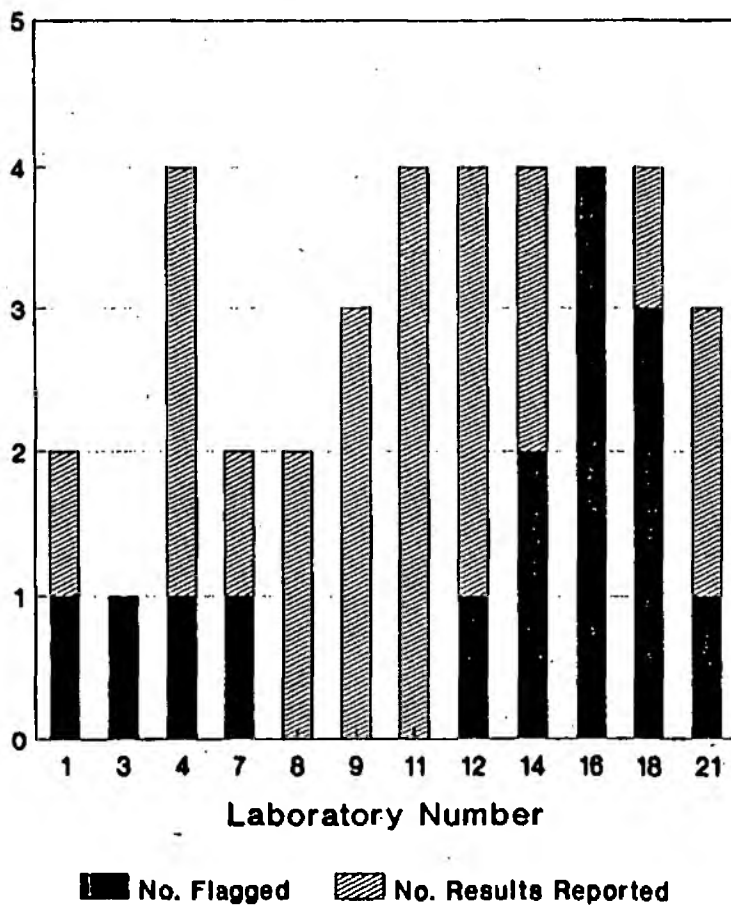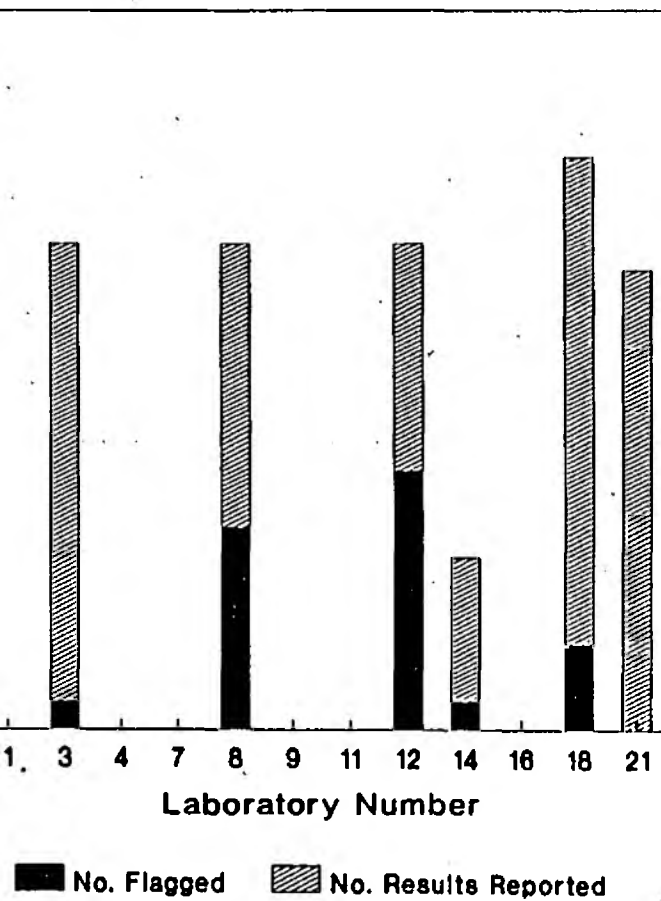
OVERALL LABORATORY PERFORMANCE IN THE FOUR DISTRIBUTIONS IN YEAR 1 FOR ALL MATRICES (AQUEOUS, SEDIMENT, BIOTA)

LAB NO.	NO. REPORTED DATA	NO FLAGGED DATA	% RETURNS	% PASSES
1	90	31	28.4	65.6
2	78	13	24.6	83.3
3	121	26	38.2	78.5
4	213	55	67.2	74.2
5	79	7	24.9	91.1
6	24	1	7.6	95.8
7	188	57	59.3	69.7
8	68	22	21.5	67.7
9	54	18	17.0	66.7
10	87	42	27.5	51.7
11	134	33	42.3	75.4
12	281	54	88.6	80.8
13	48	9	15.1	81.3
14	122	30	38.5	75.4
15	195	36	61.5	81.5
16	65	29	20.5	55.4
17	92	28	29.0	69.6
18	278	47	87.7	83.1
19	209	21	65.9	90.0
20	37	2	11.7	94.6
21	143	29	45.1	79.7
22	0	0	-	-

Maximum determinands possible = 317

NATIONAL MARINE AQC SCHEME
MARINE METHODS

KEY

Please use the following codes to complete the boxes:-

- Current AQC status (Internal)

- Current AQC status (External)

INTERNAL AQC; GIVE THE CURRENT STATUS OF YOUR METHOD USING ONE OF THE FOLLOWING CATEGORIES:

1. Precision and bias testing carried out.

2. Precision and bias testing for the method carried out and control charts in use.

3. Precision, bias testing and recovery tests carried out and control charts in use.

4. As for category 2, plus certificated reference materials in use.

5. As for category 3, plus certificated reference materials in use.

6. Others, please specify.

EXTERNAL AQC; GIVE THE CURRENT STATUS OF YOUR METHOD USING ONE OF THE FOLLOWING CATEGORIES:

1. Routine inter-laboratory tests carried out within your organisation (or locally).

2. Routine inter-laboratory tests carried out nationally, eg. Aquacheck, UK Marine AQC.

3. National or International one-off inter-laboratory comparison tests carried out, eg. ICES, JMG.

4. Others, please specify.

One sheet per determinand or group of determinands to be completed. Please return to Dr. A.H. Griffiths, Forth River Purification Board, Heriot-Watt Research Park, Avenue North, Riccarton, Edinburgh, EH14 4AP, by 21st November, 1992.

Substances determined:
Type of Sample:
Principle of the method:
Limit of Detection (LoD):
Basis of LoD calculation:
Normal Operating Ranges:
Current AQC status (Internal) - see attached key:
Current AQC status (External) - see attached key:
Literature Reference:
Laboratory name & address:

EXAMPLE

National Marine AQC Scheme
Marine Methods

One sheet per determinand or group of determinands to be completed. Please return to Dr. A.H. Griffiths, Forth River Purification Board, Heriot-Watt Research Park, Avenue North, Riccarton, Edinburgh, EH14 4AP, **by 21st November, 1992.**

Substances determined:	Orthophosphate
Type of Sample:	Seawater (Estuarine & Marine)
Principle of the method: The seawater is allowed to react with a composite reagent containing molybdic acid , ascorbic acid and trivalent antimony. The resulting complex heteropoly acid is reduced in situ to give a blue solution the extinction of which is measured at 885nm.	
Limit of Detection (LoD): 0.02µm	
Basis of LoD calculation: 4.65 x within batch standard deviation of single blank determinations	
Normal Operating Ranges: 0.02 - 5 µm	
Current AQC status (Internal) - see attached key: 2	
Current AQC status (External) - see attached key: 2	
Literature Reference: Murphy and Riley (Anal.Chim. Acta, 27:31, 1962)	
Laboratory name & address: As appropriate	

Thank you for taking the time to complete the method sheet.

AHG/SG/STN-3/KP/TBLS/AQC

MARINE METHODS : AMMONIA

LABORATORY	METHOD IN USE	REPORTED LoD	OPERATIONAL RANGE	INTERNAL AQC STATUS
1 and 2	Indophenol blue 660 nm	1 μg/l 0.01 mg/l	0-60 μg/l 0-2 mg/l	2
3	Indophenol blue Automated, 630 nm			
4	Indophenol blue 640 nm	0.01 μM	0.1-25 μM 2	2
5* and 8	Indophenol blue 630 nm	0.15 μM	0.15-15 μm	2
6				
7	Indophenol blue 635 nm	0.3 μM	0.3-56 μM	
9				
10	Under development			
11				
12*	Indophenol blue Automated, 630 nm	4 μg/l	0-25 μg/l	3
14	Indophenol blue	0.05 μM	0.1-4° μM	1
15	Indophenol blue	3.84 ?	0-500 μg/l	3
16	Indophenol blue	0.0026 mg/l	0.0026-0.2 mg/l	3
18	Indophenol blue	0.39 μM	0.39-28.6 mg/l	3
19		0.39 μM	0.39-28.6 μM 14.3-114.3 μM	3

KEY

Internal AQC Status - see Appendix 5.2.1 (1)

* Passed in both distributions 1 and 2 (Groups 1 and 2)

MARINE METHODS : ORTHOPHOSPHATE

LABORATORY	METHOD IN USE	REPORTED LoD	OPERATIONAL RANGE	INTERNAL AQC STATUS
1 and 2	Phosphomolybdenum complex 880 nm	1 μg/1 0.01 mg/1	0-30 μg/1 0-1 mg/1	2
3	Phosphomolybdenum complex 882 nm	0.01 μM		
4*	Phosphomolybdenum complex 885 nm	0.01 μM	0.01-3 μM	2
5* and 8	Phosphomolybdenum complex 885 nm	0.03 μM	0.03-3 μm	2
6				
7*	Phosphomolybdenun complex	0.06 μM	0.03-5 μM	2
9				
10				
11				
12*	Phosphomolybdenum complex Automated 885 nm	1 μg/1	0-100 μg/1	3
14	?	0.01 μM	0.01^{-2} μM	1
15				
16	Phosphomolybdenum complex	0.0042 mg/1	0.0026-0.2 mg/1	3
18				
19*				

KEY

Internal AQC Status - see Appendix 5.2.1 (1)

* Passed in both distributions 1 and 2 (Groups 1 and 2)

MARINE METHODS: TON

Laboratory	Method in Use	Reported LoD	Operational Range	Internal AQC Status
1 and 2	Cadmium reduction. Diazotisation at pH = 1.9 540 nm. Nitrate by difference	0.1mg/l as N	0 - 20 mg/l as N	2
3	As for laboratory 1 and 2 543 nm - automated	-	-	-
4	As for laboratory 3 Manual	0.2 μm	0.2 - 50 μm	2
5 and 8	As for laboratory 1 and 2. 550 μm	0.07 μm	0.07 - 30 μm	2
7	As for laboratory 4	0.66 μm	0.05 - 45 μm	3
10	Under development			
12	As for laboratory 3. 550 nm	3 μg/l	0 - 200 μg/l	3
14	As for laboratory 1 and 2	0.05 μm	0.1 - 20 μm	1
15	As for laboratory 1 and 2	0.06	0 - 5 mg/l	3
16	As for laboratory 1 and 2	0.0014 mg/l	0.0014 - 0.25 mg/l	3
18	As for laboratory 1 and 2. Automated	0.167 μm	0.167 - 286 μm 14.3 - 114.3 μm	3
19*	As for laboratory 1 and 2. Automated 550 nm	0.1 μm	0.1 - 100 μm	2
11	Continuous flow	5 μg/l	0 - 100 μg/l	2

KEY   Internal AQC status - see Appendix 5.2.1 (1)

*   Passed in both distributions 1 and 2 (Groups 1 and 2)

MARINE METHODS: NITRITE

Laboratory	Method in Use	Reported LoD	Operational Range	Internal AQC Status
1 and 2 *	Diazotisation at pH = 1.9. Azo-dye at 540 nm	0.01 mg/l as N	0 - 1 mg/l as N	2
3	As for laboratory 1 and 2 543 nm - automated	-	-	-
4 *	As for laboratory 3 Manual	0.01 μm	0.01 - 3 μm	2
5 * and 8	As for laboratory 1 and 2. 550 nm	0.033 μm	0.033 - 4 μm	2
7	As for laboratory 3	0.38 μm	0.01 - 2.5 μm	2
10	Under development			
12 *	As for laboratory 3. 550 nm	0.6 ng/l	0 - 20 μg/l	3
14	As for laboratory 1 and 2	0.02 μm	0.05 - 1 μm	1
15 *	As for laboratory 1 and 2	0.48	0 - 200 μg/l	3
16	As for laboratory 1 and 2	0.0008 mg/l	0.0008 - 0.1 mg/l	3
18 *	As for laboratory 1 and 2. Automated	0.021 μm	0.021 - 7.1 μm	3

KEY   Internal AQC status - see Appendix 5.2.1 (1)

*   Passed in both distributions 1 and 2 (Groups 1 and 2)

MARINE METHODS: SILICATE

Laboratory	Method in Use	Reported LoD	Operational Range	Internal AQC Status
1 and 2	Blue silico-molybdate complex.	0.1mg/l as SiO_2	0 - 10 mg/l as SiO_2	2
3	As for laboratory 1 and 2 810 nm - automated	-	-	-
4 *	As for laboratory 1 and 2 Manual	0.1 μm	0.1 - 25 μm	2
5 * and 8	As for laboratory 1 and 2. 800 nm	0.06 μm as SiO_2	0.06 - 15 μm as SiO_2	2
7 *	As for laboratory 1 and 2 810 nm	0.62 μm	0.1 - 140 μm	2
10	Under development			
12 *	As for laboratory 3. 660 nm	4 μg/l	0 - 500 μg/l	3
14	As for laboratory 1 and 2	0.05 μm	0.1 - 30 μm	1
15 *	As for laboratory 1 and 2	0.07	0 - 5 mg/l	3
16	As for laboratory 1 and 2	0.0018 mg/l	0.018 - 10 mg/l	2
18	As for laboratory 1 and 2. Automated 820 nm	6.3 μg/l SiO_2 39.3 μg/l SiO_2	0.1 - 10 μm 5 - 40 μm	3
19	As for laboratory 1 and 2. 660 nm. Automated	1.0 μm	1 - 100 μm	2

KEY   Internal AQC status - see Appendix 5.2.1 (1)

*   Passed in both distributions 1 and 2 (Groups 1 and 2)

MARINE METHODS : TRACE METALS AQUEOUS Cu, Pb, Zn, Ni, Cd

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	Chelation with SDDC at pH 6. Extraction in chloroform. FAAS on acid extract	0.1 μg/l for Cd, Cu 5 μg/l for Pb 1.5 μg/l for Ni	0.1-11.1 μg/l 5-111 μg/l 1.5-55 μg/l	2
3	Extraction into Freon. APDC/DDDC. FAAS on acid extract (HNO₃). Ammonium dihydrogenortho-phosphate modifer	0.1 μg/l for Cu 0.06 μg/l for Pb 0.2 μg/l for Zn 5 ng/l for Cd	0.1-10 μg/l 0.06 - 1 μg/l 0.2 - 20 μg/l 5 - 200 ng/l	4
4	Extraction into Freon. APDC/DDDC. GFAAS on acid extract (HNO₃)	0.04 μg/l, Cu 0.06 μg/l, Pb 0.04 μg/l, Zn 0.02 μg/l, Cd	0.04 - 2 μg/l 0.06 - 1 μg/l 0.04 - 5 μg/l 0.02 - 0.1 μg/l	5
7	Chloroform extraction. APDC. Flame AAS on acid extract (HCl)	0.19 μg/l, Cu 0.27 μg/l, Pb 0.12 μg/l, Zn 0.05 μg/l, Cd	0.19 - 21 μg/l 0.27 - 4.6 μg/l 1.5 - 25 μg/l 0.05 - 0.31 μg/l	5
10	ASV	0.05 μg/l, Cd 1 μg/l, Pb 1 μg/l, Zn	0.05 - 5 μg/l 1 - 10 μg/l 1 - 100 μg/l	2
10	CSV, 8 hydroxy-quinoline	1 μg/l, Cu 1 μg/l, Ni	1 - 50 μg/l 1 - 60 μg/l	2
11	ICP-MS	-	-	-
12	Stripping Voltametry	0.05 μg/l, Cu 0.06 μg/l, Ni 0.05 μg/l, Cd 0.024 μg/l,Pb	0 - 10 μg/l 0 - 5 μg/l	2
15	Extraction with Trichloroethane. APDC. Then FAAS. (furnace)	0.11 μg/l, Cd 0.35 μg/l, Cu 0.25 μg/l Pb 0.23 μg/l, Ni 0.59 μg/l, Zn	0 - 1.2 μg/l 0 - 6 μg/l 0 - 6 μg/l 0 - 6 μg/l 0 - 6 μg/l	5
18	Acid sample, indium spiked. ICP-MS. Zn, Cu, Cr, Pb, Ni, Cd	1.0 μg/l 0.1 μg/l	0 - 1 μg/l	3
19	Freon extraction of dithiocarbamate derivative. AAS analsyis of acid extract (HNO₃)	0.035 μg/l, Cd 0.75 μg/l, Pb 2.6 μg/l, Zn 0.65 μg/l, Cu 0.5 μg/l, Ni	0.035 - 0.5 μg/l 0.75 - 5 μg/l 2.6 - 50 μg/l 0.65 - 10 μg/l 0.5 - 10 μg/l	6

KEY

Internal AQC Status - see Appendix 5.2.1 (1)

MARINE METHODS : AQUEOUS METALS
MERCURY AND ARSENIC

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	Sodium borohydride/Mercury vapour/Gold foil CVAAS. Argon gas.	0.02 µg/l	0.02 - 2 µg/l	2
	KI → As (V) to As (III). Sodium borohydride. CVAAS. Argon gas	0.2 µg/l	0.2 - 10 µg/l	2
4	Br/BrO₃ acid oxidation. Hydroxylammonium chloride, produces Hg (0). Gold foil CVAFS	1 ng/l	1 - 10 ng/l	2
7	HNO₃/dichromate then Br/BrO₃ acid oxidation. Hydroxylammonium chloride, produces Hg(O). Gold foil, CVAAS	4 ng/l	0 - 40 ng/l	5
11	Acid/persulphate digestion. CVAAF (Hg)	0.1 µg/l	0 - 2 µg/l	3
	Oxidation with HNO₃. Dissolution in HCl. Hydride AAS (Arsenic)	1 µg/l	0 - 40 µg/l	3
12	Stannous chloride CVAFS	8 ng/l	0 - 250 ng/l	2
15	Bromine oxidation. Stannous chloride reduction then flameless AFS (Hg)	0.01 µg/l	0 - 0.4 µg/l	5
16	Automated CVF (Hg)	0.02 µg/l	0.02 - 50 µg/l	2
18	Total mercury. Bromide/bromate oxidation Stannous chloride and CVAF.	5 ng/l	0 - 100 ng/l	-
19	Bromide/Bromate then Stannous chloride. Then CVAF.	0.03 µg/l	0.03 - 0.3 µg/l	6

KEY

Internal AQC Status - See Appendix 5.2.1 (1)

MARINE METHODS : AQUEOUS
CHROMIUM

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	Direct injection graphite furnace. AAS	0.5 µg/l	0.5 - 25 µg/l	2
4	Coprecipitation onto hydrous iron oxide. Filtration. Dissolve in HCl. Then GFAAS	0.02 µg/l	0.02 - 1 µg/l	4
10	Cathodic Stripping Voltammetry. DTPA	1 µg/l	1 - 50 µg/l	2
12	Graphite furnace AAS	0.35 ng/l	0 - 8 µg/l	2
18	Acid Sample, Indium Spiked ICP-MS	1.0 µg/l	0 - 1 mg/l	3

MARINE METHODS : AQUEOUS ORGANICS

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	Extraction into hexane. ECD and Capillary GC. GC-MS for HCB, HCBD	3 ng/l, γ-HCH 50 ng/l, α-HCH 50 ng/l, HCB 70 ng/l, HCBD	3 - 400 ng/l 50-20,000 ng/l	2 2
3	Extraction into hexane or hexane/acetone. Alumina/Silica clean up HPGC GC/MS	-	-	5
4	Extract into hexane. Alumina/silica clean-up. Capilliary GC and ECD	1 ng/l, γ-HCH 2 ng/l, Drins 3 ng/l, PCBs	1 - 10 ng/l	3
11	Hexane extraction. GC with ECD. Confirmation by GC-MSD	2 ng/l, DDTs 1 ng/l, PCBs 1 ng/l, HCHs	0 - 120 ng/l 0 - 80 ng/l 0 - 40 ng/l	2
12	Double solvent extraction with DCM. GC-MS (HCBD, HCB, γ-HCH, γ-HCH)	5 ng/l	5 - 1500 ng/l	2
14	Extraction wth hexane. Alumina/silica clean-up. GC-ECD. (HCHs and HCB)	1.5 ng/kg	1.5-750 ng/kg	1
15	Hexane extraction. Alumina silver/nitrate clean-up. Dual column ECD-GC (HCBD) αHCH, γ-HCH, HCB	2 ng/l 0.5 ng/l	2 - 10 ng/l 0.5 - 20 ng/l	3 3
16	Solvent extraction GC/ECD	0.04 ng/l, HCB 3.6 ng/l, Lindane 0.34 ng/l, HCBD	LOD - 40 ng/l	1
18	Hexane extraction. GC-ECD. Clean-up where appropriate, Alumina/silver nitrate. GC-MS (OCs and PCBs)	1 ng/l	1 - 50 ng/l	5
19	Hexane extraction. Nitrogen Blowdown. Clean-up using alumina/silica. GC-ECD (αHCH, γHCH, HCB)	1 ng/l	0 - 50 ng/l	1

KEY

Internal AQC Status — See Appendix 5.2.1 (1)

MARINE METHODS : AQUEOUS VOLATILES
CHLOROFORM AND CARBON TETRACHLORIDE

Laboratory	Method in Use	Reported LOD	Operational Range	Interal AQC Status
1 and 2	Purge and Trap. Backflush with Helium. PID and ECD detection.	0.1 µg/l	0.1 - 50 µg/l	2
11	Pentane extraction, GC/ECD	-	0 - 40 µg/l	2
12	Purge and Trap. Capillary GC/ECD	0.05 µg/l	0.05 - 10 µg/l	2
15	Purge and Trap -GC (chloroform) (carbon tetrachloride)	0.2 µg/l 0.1 µg/l	0.2 - 3.7 µg/l 0.1 - 0.8 µg/l	3
18	Pentane extraction. GC-ECD or Purge and trap. GC-MS	0.1 µg/l 2.6-16.2 ng/l	0.1 - 25 µg/l up to 1500 ng/l	5 5
19	Static headspace. Manual GC injection GC-ECD. Chloroform Carbon tetrachloride	0.5 µg/l 0.1 µg/l	0.5 - 50 µg/l 0.1 - 5 µg/l	2

KEY

Internal AQC Status – See Appendix 5.2.1 (1)

MARINE METHODS, AQUEOUS PCP

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	Acid extraction into hexane. Dried and reacted with diazomethane. GC-MS. Internal C_{13} -PCP standard	0.1 µg/l	0.1 - 50 µg/l	2
4	PCP derivatised to phenylacetate, with acetic anhydride. Extract into hexane. Capillary GC and ECD.	0.02 µg/l	0.02 - 0.2 µg/l	3
11	Derivatisation with pentafluorobenzyl chloride. Hexane extraction. GC-MSD	0.2 µg/l	0 - 10 µg/l	2
12	Hexane extraction (pH 2-3). Derivatisation with diazomethane. GC-MS	0.05 µg/l	0.1 - 5 µg/l	2
14	Hexane extraction (acid/base). Methylation. GC-ECD. Internal standard.	1.5 ng/kg	1.5 - 750 ng/kg	1
15	Solvent extraction. Derivatisation with α-bromo-pentafluorotoluene. GC-MS.	50 ng/l	50 - 250 ng/l	3
18	Diethyl ether extraction. Methylation. GC-ECD. Clean-up where appropriate Alumina/silver nitrate	0.01 µg/l	0.01 - 0.25 µg/l	5
19	Acetic Anhydride derivatisation. Extract into hexane. GC-ECD	100 ng/l	100 - 2000 ng/l	1

KEY

Internal AQC Status — See Appendix 5.2.1 (1)

MARINE METHODS : SEDIMENTS METALS
Cu, Pb, Zn, Ni, Cd, Cr

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	Wet oxidised with conc HNO₃, AAS	1.5 mg/kg Cu 5 mg/kg Pb 0.5 mg/kg Cd, Zn 3 mg/kg Ni 10 mg/kg Cr	5 - 2000 mg/kg dry wt	4
3	HNO₃/HCl extraction, room temperature, then heated. Then flame AAS.	0.006 ppm Zn 0.06 ppm Ni 0.01 ppm Cu 0.05 ppm Cr 0.006 ppm Cd	0.1 - 10 ppm Zn 0.06 - 5 ppm Ni 0.01 - 5 ppm Cu 0.05 - 5 ppm Cr 0.006-5 ppm Cd	4
3	HF/Aqua Regia Microwave digestion. Boric acid. Flame and FAAS.	0.05 ppb Cd 0.01 ppm Cu 0.05 ppm Cr 0.06 ppn Ni 1 ppb Pb	0.05 - 3 ppb 0.01 - 5 ppm 0.05 - 5 ppm 0.06 - 5 ppm 1 - 60 ppb	4
4	HNO₃ digestion microwave. Then AAS or Furnace AAS.	0.05 µg/g Cu 0.05 µg/g Cd 0.05 µg/g Cr 0.3 µg/g Pb 0.05 µg/g Ni	0.05 - 50 µg/g 0.05 - 0.5 µg/g 0.05 - 100 µg/g 0.3 - 100 µg/g 0.05 - 50 µg/g	2
6	DC arc emission spectroscopy	5 µg/g Cu 10 µg/g Pb 0.8 µg/g Cd 15 µg/g Zn	5 - 500 µg/g 10 - 1000 µg/g 0.8 - 10 µg/g 15 - 2000 µg/g	1
6	HF digestion then ICP - AES	3 µg/g Cu 18 µg/g Pb 3 µg/g Cd 8 µg/g Zn	5 - 500 µg/g 10 - 1000 µg/g 0.8 - 10 µg/g 15 - 2000 µg/g	1
9	Digestion with 32% Aqua Regia, Reflux ICP-DES	0.06 mg/kg Cd 0.8 mg/kg Cr 0.3 mg/kg Cu 2.1 mg/kg Pb	0.5-1000 mg/kg 5 - 500 mg/kg 5 - 1000 mg/kg 5 - 1000 mg/kg	4
11	Microwave digestion. Flame AAS or furnace AAS. Zeeman correction.	0.1 mg/kg Cu 0.1 mg/kg Pb 0.05 mg/kg Cd 0.1 mg/kg Cr	-	4
12	Aqua regia digestion. ICP-MS	0.3 mg/kg Cd 2 mg/kg Cu 2 mg/kg Pb 2 mg/kg Zn 3 mg/kg Cr	0 - 200 mg/kg	2

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
14	Aqua regia microwave digest. HF solubilisation second step. Boric acid. Then flame AAS.	1.0 µg/g	1 - 100 ppm	2
18	Microwave digestion with HCl and HNO_3. ICP-MS	0.005 mg/l Cd 0.05 mg/l Cr 0.05 mg/l Cu 0.05 mg/l Pb 0.1 mg/l Zn	5 mg/l	-
19	Aqua Regia reflux for 2 hours. Then AAS	0.2 mg/kg Cd 0.6 mg/kg Cu 1 mg/kg Pb 0.6 mg/kg Ni 0.2 mg/kg Zn 0.8 mg/kg Cr	0.2 - 20 mg/kg 0.6 - 100 mg/kg 1 - 100 mg/kg 0.6 - 100 mg/kg 0.2 - 50 mg/kg 0.8 - 100 mg/kg	6

KEY

Internal AQC Status – See Appendix 5.2.1 (1)

MARINE METHODS : SEDIMENT
MERCURY, ARSENIC

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
1 and 2	High pressure digestion with Aqua-regia. Then CVAFS	0.01 mg/kg Hg 0.1 mg/kg As	0.02-2 µg/l Hg 0.2-10 µg/l As	4
3	HNO₃/HCl extraction-room temperature, then heated. CVAFS.	0.001 ppm Hg	0.001 - 40 ppm Hg	4
3	HF/Aqua Regia Microwave digestion. Boric acid. Then CVAFS.	0.001 ppm Hg	0.001-4 ppm Hg	4
4	Microwave digestion with HNO₃. Tin chloride. Then CVAFS. As above, sodium borohydride then AAS	10 ng/l Hg -	0.5-6 µg/g Hg 4 µg/g As	5
6	Acid permanganate; tin chloride. Gold foil then CVAAS	10 µg/g Hg	-	1
9	Digestion with 32% Aqua Regia. CVAAS Digest with HNO₃. Ashed with magnesium nitrate, Hydride generation, AAS	0.05 mg/kg Hg 1 mg/kg As	0.05 -1 mg/kg Hg 1 - 8 mg/kg As	4 4
11	Microwave digestion. CVAAF Hydride generation. Digestion as above	0.05 mg/kg Hg 0.5 mg/kg As	- -	4 4
14	Aqua regia microwave digest. HF solubilisation. Second step Boric acid. Then CVAAS	0.05 µg/g Hg 0.1 µg/g As		2
18	Microwave digestion with HCl and HNO₃. ICP-MS. Then stannous chloride and AF KI/Boron hydride →AAS	0.05 µg/l Hg 1 mg/l As	up to 10 µg/l up to 2 mg/l	-
19	Aqua Regia digest. Then AFS	0.025 µg/g Hg	0.025-50 µg/g	5

KEY

Internal AQC Status — See Appendix 5.2.1.(1)

MARINE METHODS : SEDIMENTS ORGANICS

Laboratory	Method in Use	Reported LOD	Operational Range	Internal AQC Status
3	Soxhlet Extraction: Hexane or Hexane/Acetone. Alumina/Silica clean-up. HPGC and GC/MS.	0.001 ppm wet weight	sub ppm → hundreds ppm	5
11	Hexane extraction. GC/ECD. Confirmation by MSD for HCBD	0.4 µg/kg, DDTs 0.2 µg/kg, PCBs 0.2 µg/kg, HCB	Various	4
14	Soxhlet extraction with DCM. Alumina/silica clean-up. GC-ECD. Internal standard (HCB, Dieldrin, DDTs)	0.01 µg/kg	0.01-500 µg/kg	3
	As above (chlorobiphenyls)	0.01 µg/kg	0.01-500 µg/kg	5
15	Hexane extraction. Alumina/silver nitrate clean-up. Dual column ECD-GC pp-DDT Dieldrin, DDTs, Drins (propanol/hexane extraction) PCBs pp DDE	1.2 µg/kg 1.2-2 µg/kg 5-7.5 µg/kg 0.7 µg/kg	1.2-20 µg/kg 1.2-50 µg/kg 5 - 100 µg/kg 0.7-20 µg/kg	3 3 5 3
18	Soxhlet extraction into Acetone/hexane. Clean-up using alumina/silver nitrate GC-ECD. GC-MS	-	-	5
19	Soxhlet extraction Acetone/hexane. Aluminia clean-up/silical gel. Sulphur removal alumina/silver nitrate GC/ECD. (PCBs, HCB, Drins, DDTs)	1 µg/kg	0-100 µg/kg	1

KEY

Internal AQC Status – See Appendix 5.2.1 (1)