

**REPORT ON THE NATIONAL MARINE CHEMICAL ANALYTICAL  
QUALITY CONTROL SCHEME 2002**

**Presented to the June 2003 Meeting of the National Marine Monitoring  
Programme Working Group**

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# NATIONAL MARINE CHEMISTRY ANALYTICAL QUALITY CONTROL SCHEME

## REPORT FOR THE PERIOD DECEMBER 2001 – DECEMBER 2002

### EXECUTIVE SUMMARY

This is the eighth report of the National Co-ordinating Committee (NCC) of the National Marine Chemical AQC scheme (NMCAQC). The report describes the actions taken during the above period to ensure the quality assurance of data submitted to the UK National Marine Monitoring Programme (NMMP).

The report includes the results of the implementation and operation of the Data Filter for data submitted to the temporal trend monitoring phase of NMMP II.

The data filter process has shown that, for a very large proportion of NMMP II data, contributing laboratories can provide a demonstration that they satisfy the basic NMMP performance requirements. Despite this, there are areas where improvements are desirable (both in performance achieved and in the extent to which performance can be demonstrated). The main areas where fitness for purpose is not consistently achieved by laboratories is for the determination of organochlorine substances and polycyclic aromatic hydrocarbons in biota.

During the period of this report, the NCC has:

- Ensured that the quality standards achieved in previous years are maintained
- Ensured scope of the scheme has been maintained, through membership of the QUASIMEME Advisory Board
- Encouraged a continuing Quality Assurance approach to managing laboratory analytical performance through routine distributions, special exercises and workshops
- Maintained prudent financial management of the scheme
- Implemented a new Data Filter for NMMP II data
- Summarised contaminant data for the 2<sup>nd</sup> NMMP report

Future NCC activities will include:

- Maintenance and development of the Quality Assurance approach through continuing routine proficiency testing, special exercises and workshops.
- Ensuring that laboratories have Quality Assurance in place as new determinands are introduced to the NMMP e.g. organo tin in sediments.
- Developing QC protocols for field instrumentation.
- Review of Quality Assurance of sampling and sample handling.
- Ensuring suitable test materials are suitable for all matrices in the NMMP.

## TABLE OF CONTENTS

EXECUTIVE SUMMARY .....	2
TABLE OF CONTENTS .....	3
APPENDICES .....	4
LIST OF TABLES .....	4
GLOSSARY OF TERMS .....	5
1. INTRODUCTION .....	6
1.1 Participating Laboratories .....	6
2. REPORT OF THE NATIONAL CO-ORDINATING COMMITTEE .....	7
2.1. NCC Activities .....	7
2.2 NMCAQC Finances .....	8
3. QUASIMEME PROGRAMME .....	8
3.1 Routine Programme .....	8
3.2 Development exercises .....	8
4. Performance Indicators .....	8
6. Assessment of Laboratories Performance .....	11
7. LABORATORY IMPROVEMENT PLANS .....	13
8. WORKSHOPS .....	13
9. SAMPLE HANDLING & SAMPLE PRESERVATION .....	13

## **APPENDICES**

APPENDIX 1.1 Laboratories Participating in the NMCAQC Scheme

APPENDIX 1.2 Laboratories Analysing NMMP samples

APPENDIX 2.1 Membership of the National Co-ordinating Committee

APPENDIX 2.2 NMCAQC Financial Summary

APPENDIX 3.1 QUASIMEME Programme

APPENDIX 6.1 Percentage of accepted data

APPENDIX 6.2 PT performance

APPENDIX 6.3 PT results for metals and organics in water

APPENDIX 6.4 Range of PT scores

APPENDIX 7. Laboratory Improvement Plans

APPENDIX 8.1 Summary of Chlorophyll Workshop

APPENDIX 8.2. Summary of TBT Workshop

## **LIST OF TABLES**

Table 5.1. Data Filter Criteria.

## **GLOSSARY OF TERMS**

NMCAQC	National Marine Chemical Analytical Quality Control
AQC	Analytical Quality Control
DARDNI	Department of agriculture and rural development (Northern Ireland)
SEPA	Scottish Environment Protection Agency
EHS	Industrial research and technology Unit
LOD	Limit of Detection
CEFAS	Centre for Environment Fisheries and Aquaculture Science
MPMMG	Marine Pollution Monitoring Management Group
NCC	National Co-ordinating Committee
NLS	National Laboratory Service (EA)
NMMP11	National Marine Monitoring Programme - Phase 11
NMMP	National Marine Monitoring Programme
EA	Environment Agency
NCEDS	National Centre for Environmental Data and Surveillance
QUASIMEME	Quality Assurance of Marine Environmental Monitoring in Europe
FRS	Fisheries Research Services
DEFRA	Department of the Environment, Fisheries and Rural Affairs
WRc	Water Research Centre
NMMPWG	National Marine Monitoring Programme Working Group
QA	Quality Assurance
QUASH	Quality Assurance of Sampling and Sample Handling
PCBs	Poly-chlorinated biphenyls
TON	Total oxidised Nitrogen
EHS	Environment and Heritage Service
PAH	Polycyclic Aromatic Hydrocarbons

## 1. INTRODUCTION

This report covers the activities of NMCAQC in 2002. During this time the NMCAQC Scheme has continued to pursue its aims and objectives, namely:

- (i) To monitor and demonstrate the analytical accuracy achieved by laboratories which contribute data to the National Marine Monitoring Programme (NMMP);
- (ii) To collate information on standards of accuracy achieved for NMMP determinands, to provide a screening tool for data submitted to the NMMP database; and
- (iii) To assist in achieving improved standards of accuracy, where appropriate.

These aims and objectives are addressed through three types of activity:

### **a) proficiency tests**

Laboratories are required to take part in an interlaboratory proficiency test at least twice per year for all determinands for which they report data to the NMMP. These tests provide a continuing check on comparability for the determinands and matrices required for the NMMP.

### **b) special exercises for important or "problem" determinands**

These are series of interlaboratory tests, which are intended to assist in the development of laboratories' systems, and in achieving an improvement in performance where accuracy and/or precision falls short of that required.

### **c) training workshops**

Training workshops are organised to exchange information concerning best analytical practices. The workshops are co-ordinated with the programme of special exercises.

Proficiency test samples, special exercises and training workshops are provided by the QUASIMEME interlaboratory proficiency test scheme.

## **1.1 Participating Laboratories**

All laboratories that submit data to the NMMP participate in the NMCAQC scheme. A list of laboratories participating in the NMCAQC Scheme is given in Appendix 1.1 and a summary table showing where NMMP samples are analysed is given in Appendix 1.2.

This report is intended to inform the NMMP Working Group of the steps taken by participating laboratories to assure the quality of the data collected as part of the NMMP. It covers data generated for the third year of phase II of the NMMP.

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

### **2.1. NCC Activities**

The current membership is shown in Appendix 2.1. Lynda Webster joined the group to represent FRS, there were no other changes in 2002.

The NCC continues to promote participation in external interlaboratory proficiency testing schemes whilst maintaining in-house AQC as a continuing check of daily performance. The international interlaboratory proficiency testing scheme QUASIMEME continues to be the main provider of external QC. Laboratories purchase proficiency test samples direct from QUASIMEME and receive their results back from QUASIMEME. Laboratories are then required to forward these results to the NMCAQC database at the EA National Centre for Environmental Data and Surveillance (NCEDS) at Twerton. The Chairman of the NCC sits on the QUASIMEME Advisory Board to ensure that external AQC is available for all determinands in NMMP.

The main activities of the NCC throughout the period have been:

1. Implementing a new data filter for 1999-2001 data.
2. Organisation of workshops.
3. Summarising 1999-2001 contaminant data for the 2<sup>nd</sup> NMMP report.
4. Agreeing performance indicators for contaminant data for use in the 2<sup>nd</sup> NMMP report.

The group has continued to focus on the agreed remit:

#### **1. Remit from NMMP Working Group**

The group's remit is to provide quality assurance (QA) for all the marine chemistry data submitted as part of the NMMP programme. The group need to maintain and, where necessary, improve the current level of QA, and ensure that provision is made for areas not currently covered. NMCAQC needs to objectively evaluate laboratories' performance, and ensure that where necessary, appropriate measures are put in place to enable laboratories to improve their performance.

#### **2. Full participation of individuals and organisations**

Participation in the group should include work by each member throughout the year, and not just at NCC meetings, and it is hoped that organisations will support the members in this. NCC representatives should in addition look for opportunities for individual or small group work on particular topics, to help the group to progress issues.

#### **3. The wider view**

The group needs to maintain a wider view on developments in Marine Chemistry, particularly in Europe. Much of this is key to focused delivery of its main remit. Future developments include topics under discussion by OSPAR, work on "new" substances (brominated flame retardants), the need for the development of

standards (e.g. for eutrophication assessment), environmental indicators, and background and reference concentrations, and the need to improve links with other disciplines (e.g. biological effects) to add value to chemistry results.

## **2.2 NMCAQC Finances**

Since 1997 laboratories have purchased test materials direct from QUASIMEME and paid a small annual subscription to NMCAQC to fund consultants and contracts. Laboratories submitting data to the NMMP were not asked for an annual subscription this year as the scheme has sufficient funds available (see Appendix 2.2). These funds are used to:

1. Provide expert advice to NCC
2. Provide funding for speakers at workshops
3. Hospitality

## **3. QUASIMEME PROGRAMME**

### **3.1 Routine Programme**

QUASIMEME continue to provide a comprehensive range of determinands covering NMMP requirements (see Appendix 3.1).

Determinand groups are distributed twice per year and there are generally two samples per group covering low range and high range concentrations. Additional high range aqueous samples were introduced in 1999/2000 to satisfy the requirements of laboratories monitoring for EQS compliance.

### **3.2 Development exercises**

QUASIMEME organises development exercises for new or problem determinands. There were 5 development exercises during 2001/2:

1. Organotins in biota, seawater and sediments (3 separate exercises). - The analysis of TBT in biota is required to complement imposex analysis and the analysis of TBT in sediments is required by OSPAR in 2003.
2. Chlorophyll a – this will become routine in 2003.
3. Brominated flame retardants – these are not currently included in NMMP II but are on the Water Framework Directive Priority list and may be in a revised JAMP.

## **4. Performance Indicators**

Following the NMMP workshop on Performance Indicators in May 2001 Defra funded a contract to develop B/RCs applicable to the UK. An initial review has been completed using Scottish data, work is continuing to broaden the applicability of the indicators throughout the UK. The proposed new B/RCs need to be agreed by



OSPAR before they can be implemented so existing OSPAR B/RCs and EACS have been used to assess data in the 2<sup>nd</sup> NMMP report.

## 5. Data Filter

A revised data filter format (see Table 5.1 below) was devised. Information requirements were modified to be shorter, more easily obtained from existing QC records and from information (largely) needed anyway for the ICES data evaluation process. These new information requirements were requested in an easily analysable spreadsheet for each laboratory, sample matrix, determinand combination. Proficiency test data was transferred to the spreadsheet from the NMCAQC database held at NCEDS. Ideally all QC information should be submitted with the contaminant information and held on the same database. It is anticipated that the data filter requirements will be incorporated into the new NMMP database.

The data interpretation was carried out on the basis of achievement of NMMP criteria for performance e.g. limit of detection, standard deviation of results, control over bias etc and for implementation of various essential aspects of quality control. The ten new criteria (i.e. questions) were compared with the previous 18 and found to place slightly more emphasis on performance achieved compared with the reliability of the demonstration of performance, but it was estimated that there was an 85% overlap between scoring for the modified and initial data filter. In other words, the revised data filter covered nearly all the same issues as the initial version (with similar weight being placed on each) and that the 15% discrepancy was accounted for by a greater score being awarded for the claim of meeting performance targets, rather than to the background data supplied to support that claim.

An acceptable score – indicative of fitness for purpose - of 40 percentage points was set for nutrients and trace metals in sediments and biota. This was on the basis of what was judged to be the minimum criteria for fit for purpose. For trace organic determinands, a threshold score of 35 was set.

**Table 5.1 Data Filter Criteria**

<b>Data Filter Criterion</b>	<b>Score %</b>
Is the laboratory accredited for the specified determinand - <i>is the lab. well organised?</i>	<b>5</b>
Is the Limit of Detection achieved consistent with NMMP requirements? (1)	<b>5</b>
Control charts - are charts plotted for the determinand in question? – <i>a key element of routine QC</i>	<b>15</b>
Comparison of control chart expected value with control chart mean value – <i>an indicator of bias.(1)</i>	<b>15</b>
Number of measurements made on control chart reference material during period of interest – <i>indicator of the power of chart to detect anomalies (2)</i>	<b>15</b>
Control chart reference material standard deviation – <i>a measure analytical precision (1)</i>	<b>10</b>
Number of measurements used to establish std devn for control chart limits – <i>reliability of sd estimate and of control limits</i>	<b>5</b>
Number of breaches of warning limits during period for which limits apply ( <i>used to assess validity of control limits</i> ) (3)	<b>0</b>
Proficiency testing (4)	<b>30</b>
<b>Total</b>	<b>100</b>

**Notes**

1. Some scores were applied in a graded manner such that failure to meet the corresponding NMMP target did not result in a zero score unless the failure was substantial. See below: Gradations in nmaq scores

**Limit of detection score**

full 5 points awarded if reported lod is less than target minimum lod  
 3 if below 1.5x target lod  
 1 if below 2.01x target lod

**Bias score**

full 15 points awarded if observed bias is less than target maximum tolerable bias.  
 10 if below 1.5x target  
 5 if below 2.01x target

**Standard Deviation score**

full 10 points awarded if reported sd is less than target maximum tolerable sd  
 7 if below 1.5x target  
 3 if below 2.0x target

2. Control chart number score – rounded from 0 to 15 in proportion to the number of points up to 40. Above 40 points score is 15.

3. The range of numbers of expected out of warning limit values was estimated, for the stated number of points plotted. This was based on binomial probability, given an assumed true compliance of 95% (ie that expected for correctly plotted limits). Thus for 30 points the expected range was between 0 and 3, for 50 points between 0 and 4, for 70 points between 1 and 7. Recorded numbers of failures outside these ranges were assigned a score of –5 points.

4. Proficiency test score – awarded from 0 to a maximum of 30 in proportion to the % pass rate in proficiency tests in which the laboratory participated (by reporting numerical data).

## 6. Assessment of Laboratories Performance

The array of scores (for each laboratory and determinand) was converted to an array of “acceptable” (i.e. fit for purpose) data by flagging only the elements of the array for which the score exceeded the thresholds noted above. This was then matched with data indicating which laboratory had reported data for which NMMP site (for the determinand in question) to produce a matrix of sites for which the data were considered fit for purpose. The outcome of this analysis was reported to the NMMP database at Twerton.

Appendix 6.1 shows the percentages of accepted data summarised by determinand class. Two points are worth noting in relation to this. Firstly, the great majority of results meet the data filter criteria (a consequence of the progress made over nearly 10 years’ QC work by the NMCAQC group). Secondly, whilst it is possible to define levels of analytical performance which, if achieved, will confer fitness for purpose on the associated data, this concept of sufficiency does not necessarily transfer to the level of quality control activity undertaken to demonstrate fitness for purpose. All aspects of QC identified in the data filter are desirable components of a sound approach to QC. The aim is not to reach a certain level of QC activity that gives a score that is just high enough to exceed the threshold; the intention is that both performance and procedures should be such that a score approaching 100% is achieved. Appendix 6.2 also shows the performance of laboratories in proficiency tests. This in general follows the picture indicated by the data filter. Where comparability is not good the reason may be that the assessment based on proficiency tests is probably less robust (ie more subject to random variations) and that some laboratories may not have taken part in a sufficient number of proficiency tests.

A quality assessment for the determination of metals and organics in seawater was performed on the earlier basis of proficiency test performance. This was because the NMCAQC group had not requested data filter information for these parameters. The outcome of this evaluation is shown in Appendix 6.3.

The range of data filter scores achieved by different laboratories for each determinand is shown in Appendix 6.4 – for the year 2000 as an example.

1. The process shows that, for a very large proportion of NMMP II data, contributing laboratories can provide a demonstration that they satisfy the basic NMMP performance requirements. Despite this, there are areas where improvements are desirable (both in performance achieved and in the extent to which performance can be demonstrated).
2. The main areas where fitness for purpose is not consistently achieved by laboratories is for the determination of organochlorine substances and polycyclic aromatic hydrocarbons in biota.

The following recommendations are listed as a record of points arising out of the discussions held during the application of 1999 Data Filter.

**Representative determinands in routine QC.** Although the use of one determinand to represent a structurally similar one was accepted in this assessment, it was felt that best practice is to undertake QC analyses for all individual determinands.

**Plotting of control charts.** It was noted that some laboratories did not produce plots of all their control chart data. It was accepted that the principal functions of a chart could be reproduced by calculations without plotting (either as an electronic graph or a hardcopy version) the chart. However, it was felt that this was likely to limit the ease of use of control data in a number of respects (notably the early identification of trends). It was considered best practice that it should be possible to carry out a visually assessment of control data.

**Fish muscle and liver.** Laboratories that report data for determinands in fish muscle and liver should consider the development of testing and routine QC programmes in these matrices. For a number of laboratories in this assessment testing and QC data relating to the analysis of shellfish have been used to support the validity of analyses in fish muscle and liver.

**Special proficiency tests.** It is recommended that steps be taken to make sure that the NMMP database of proficiency testing results includes the results of special exercises.

**Areas where improved analytical performance is indicated.** The need for improved analytical performance is best assessed by a review of laboratories' performance in proficiency testing. The great majority of low scores in the Data Filter assessment relate to determinand/matrix combinations that are not currently analysed by the laboratory concerned. It is recommended that when laboratories do implement new techniques with a view to reporting data for NMMP purposes that consideration should be given to ensuring a satisfactory datafilter score by undertaking performance tests at the outset and implementing a fully developed approach to within-laboratory QC. Determinands for which the collection of data for the Data Filter indicated either that analysis required by NMMP was not being done or that there were gaps in QC practice were: some organochlorine determinands in biota and some metals (e.g. lithium and silver in sediments).

**Support determinands.** The issue of quality assurance for the so-called support determinands was raised. These include lipids in biota, and "normaliser" parameters such as particle size determination, lipid and TOC.

**Identification of relevant time period for annual Data Filter runs.** The importance of knowing which results were relevant to each Data Filter run was noted. It was concluded that the key date that identified the appropriate Data Filter assessment was the date of laboratory analysis. Date associated with reported results – eg sampling date, date of reporting or date of entry onto the database might be of value in other contexts but they are not particularly useful in this context. It was noted that the variety of date information available on the database should be reviewed. It was agreed that the average of three years PT results be used for the data filter.

## **7. LABORATORY IMPROVEMENT PLANS**

It was agreed that individual laboratories should review their performance annually and draw up plan to improve their performance in future years in order to maximise the data on the NMMP database. Individual Laboratory Improvement Plans are provided in Appendix 7.

## **8. WORKSHOPS**

QUASIMEME hosted two workshops and held a conference in 2002. The first workshop on 1/2 July 2002 discussed the analysis of chlorophyll. This was followed on the 3/5 July by a workshop on the analysis of organotins in waters sediments and biota. Subjects discussed at the workshop are outlined in Appendix 8.1 and 8.2.

The conference in Barcelona in October reviewed laboratories performance over the 10 years of QUASIMEME. Results were similar to those obtained by the data filter exercise for UK laboratories i.e. laboratories were generally good at measuring nutrients but poor at measuring OCs in biota. A summary of the conference on CD is included in this report.

## **9. SAMPLE HANDLING & SAMPLE PRESERVATION**

This has been dealt with by the Quality Assurance of Sample Handling (QUASH) project, which received EU funding for 3 years. The main programmes of work within QUASH are:

1. Nutrients - sampling and preservation
2. Sediments - sample handling and normalisation cofactors
3. Biota - sample handling and normalisation cofactors (lipids and water)

Final reports have just become available. The recommendations will be reviewed next year and implemented as appropriate.

## **APPENDIX 1.1 LABORATORIES PARTICIPATING IN THE NMCAQC SCHEME**

BGS, KEYWORTH  
SEPA WEST, EAST KILBRIDE  
DANI AQUATIC SCI., BELFAST  
DANI FOOD & AGR., BELFAST  
SEPA EAST, EDINBURGH  
EHS, LISBURN  
CEFAS BURNHAM  
CEFAS LOWESTOFT  
ENVIRONMENT AGENCY NLS NOTTINGHAM  
ENVIRONMENT AGENCY NLS EXETER  
ENVIRONMENT AGENCY NLS LLANELLI  
ENVIRONMENT AGENCY NLS LEEDS  
FRS, ABERDEEN  
ENVIRONMENT AGENCY SHIPBOARD LABORATORIES (4)

## APPENDIX 1.2 LABORATORIES ANALYSING NMMP SAMPLES

### SEDIMENTS

Metals (total digest) Al, Cd, Hg, Cu,Pb, Ni, Zn, As, Cr, Li, Fe, Mn

Organisation	Site	QA
FRS	205, 175, 45, 55, 70, 76, 85, 95, 105, 165	MS-1
CEFAS	245, 285, 345, 475, 536, 605, 715, 775, 805	MS-1
EHS	845, 820, 880, 825	MS-1
DARD	806, 807, 808, 809, 815, 865, 875	MS-1
Llanelli	435, 455, 505, 515, 526, 527, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648	MS-1, Contest Aquacheck
Nottingham	210, 220, 225, 235, 265, 270, 275, 305, 315, 325, 356, 357, 358, 388, 389, 390, 755, 765, 766, 767,	MS-1. Contest, Aquacheck

Organics (PCB 28, 52, 101, 118, 138, 153, 180)

Organisation	Site	QA
SEPAAE	205, 175	MS-2
SEPAW	45, 55, 70, 76	MS-2
FRS	85, 95, 105, 165	MS-2
EHS	845, 820, 880, 825	MS-2
DARD	806, 807, 808, 809, 815, 865, 875	MS-2
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648, 305, 315, 325, 845, 820, 880, 825	MS-2, Contest Aquacheck
Leeds	210, 220, 225, 235, 265, 270, 275, 356, 357, 358, 388, 389, 390, 755, 765, 766, 767, 768	MS-2, Contest Aquacheck

PAH

Organisation	Site	QA
SEPAAE	205, 175	MS-3
SEPAW	45, 55, 70, 76	MS-3
FRS	85, 95, 105, 165, 845, 820, 880, 825	MS-3
DARD	806, 807, 808, 809, 815, 865, 875	MS-3
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648, 305, 315, 325,	MS-3, Contest Aquacheck
Leeds	210, 220, 225, 235, 265, 270, 275, 356, 357, 358, 388, 389, 390, 755, 765, 766, 767, 768	MS-3, Contest Aquacheck

## APPENDIX 1.2 (contd)

### SHELLFISH

Metals Hg, Cd, Cu, Pb, Ni, Zn, As, Cr, Ag, Se

Organisation	Site	QA
SEPAAE (excl As, Se)	125, 200, 207	BT-1
SEPAW	35, 45, 55, 70, 76	BT-1
FRS	Shellfish Hygiene Sites (10)	BT-1
DARD	809, 845, 880	BT-1
CEFAS	Shellfish Hygiene Sites	BT-1
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648	BT-1
Nottingham	210, 220, 225, 235, 265, 270, 275, 305, 315, 325, 330 357, 388, 389, 390, 755, 765, 766, 767, 768	BT-1

### Organics & PAH

Organisation	Site	QA
SEPAAE	125, 200, 207	BT-2/4
SEPAW	35, 45, 55, 70, 76	BT-2/4
FRS	Shellfish Hygiene Sites (10)	BT-2/4
DARD	809, 845, 880,	BT-2/4
CEFAS	Shellfish Hygiene Sites	BT-2/4
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648	BT-2
Nottingham (OCs)	210, 220, 225, 235, 265, 270, 275, 305, 315, 325, 330357, 388, 389, 390, 755, 765, 766, 767, 768	BT-2
Leeds (PAH)	210, 220, 225, 235, 265, 270, 275, 305, 315, 325, 330357, 388, 389, 390, 755, 765, 766, 767, 768	BT-4

### NUTRIENTS

Organisation	Site	QA
SEPAAE	206, 115	AQ-1, AQ-2, DE6
SEPAW	45, 55, 65, 70, 76	AQ-1, AQ-2, DE6
FRS	85, 95, 105, 165	AQ-1
EHS	845, 820, 880	AQ-1, AQ-2, DE6
DARD	806, 807, 808, 809, 815, 865, 875	AQ-1, AQ-2, DE6
CEFAS	234, 245, 295, 375, 385, 465, 475, 495, 526, 576, 585, 605, 615, 655, 665, 705, 715, 775, 785, 795, 805, 847	AQ-1
Llanelli	455, 527, 515, 565, 566, 645,	AQ-1, AQ-2, DE6
Nottingham	225, 275, 325, 356, 765, 767, 768	AQ-1, AQ-2, DE6



## APPENDIX 1.2 (contd)

### FISH

#### Metals in Muscle (As, Hg)

Organisation	Site	QA
SEPAE (Hg only)	207, 125	BT-1
SEPAW	65, 70	BT-1
FRS	85, 105, 165	BT-1
DARD	806, 807, 808, 809, 815, 820, 825, 845, 865, 875, 880	BT-1
CEFAS	244, 285, 295, 345, 486, 705, 715, 776, 785	BT-1
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648	BT-1
Nottingham	210, 220, 225, 235, 265, 270, 275, 305, 315, 325, 357, 388, 389, 390, 755, 765, 766, 767, 768	BT-1

#### Metals in liver (Cd, Pb)

Organisation	Site	QA
SEPAE	207, 125	BT-1
SEPAW	65, 70	BT-1
FRS	85, 105, 165	BT-1
DARD	806, 807, 808, 809, 815, 820, 825, 845, 865, 875, 880	BT-1
CEFAS	244, 285, 295, 345, 486, 705, 715, 776, 785	BT-1
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648	BT-1
Nottingham	210, 220, 225, 235, 265, 270, 275, 305, 315, 325, 357, 388, 389, 390, 755, 765, 766, 767, 768	BT-1

#### Organics in liver (PCB 28, 52, 101, 118, 138, 153, 180)

Organisation	Site	QA
SEPAE	207, 125	BT-2
SEPAW	65, 70	BT-2
FRS	85, 105, 165	BT-2
DARD	806, 807, 808, 809, 815, 820, 825, 845, 865, 875, 880	BT-2
CEFAS	244, 285, 295, 345, 486, 705, 715, 776, 785	BT-2
Llanelli	435, 455, 525, 526, 527, 505, 515, 555, 565, 566, 567, 576, 625, 635, 645, 690, 646, 647, 648, 305, 315, 325,	BT-2
Nottingham	210, 220, 225, 235, 265, 270, 275, 357, 388, 389, 390, 755, 765, 766, 767, 768	BT-2

## APPENDIX 2.1 NCC Membership

### NATIONAL MARINE ANALYTICAL QUALITY CONTROL SCHEME

#### NATIONAL CO-ORDINATING COMMITTEE (NCC) (2002)

Dr B Miller	(SEPA West Region)	Chairman
Mrs J Dobson	( SEPA East Region )	Fund Manager & Secretary
Mr D McMullan	( DoE NI/ EHS )	EHS Representative
Mr C Allchin	( CEFAS )	CEFAS Representative
Dr J Cook	( BGS )	BGS Representative
Mr D Wright	(EA National Marine Service)	EA NMS Representative
Dr T Oliver	( DARDNI )	DARD Representative
Mr J Fardon	( EA National Laboratory Service, Leeds)	EA NLS Representative
Dr M Gardner	( WRc )	AQC Advisor
Dr L Webster	(FRS)	FRS Representative
Dr D Wells	( QUASIMEME Project Manager)	FRS Representative

## APPENDIX 2.2 NMCAQC Financial Summary

<b>2001/02</b>			
<b>INCOME</b>		<b>EXPENDITURE</b>	
Income carried forward	£ 15428.82	Stationery	£ 59.04
Interest	£ 247.86	Hospitality	£ 273.07
Total	£ 15676.68	Total	£ 332.11
Balance carried forward	£ 15344.57		

### Appendix 3.1. QUASIMEME Programme for 2002/3

Round	Group Number	Number of test materials per exercise	Determinand Group	Matrix
<b>AQUEOUS</b>				
30 & 32	AQ-1	2	Nutrients	Seawater
30 & 32	AQ-2	3	Nutrients (low salinity, 2 high & 1 low concentration)	Estuarine and low salinity open water
31 & 33	AQ-3	3	Metals, other than Hg (includes 1 low salinity test material)	Seawater
31 & 33	AQ-4	2	Mercury	Seawater
31 & 33	AQ-5	3	Chlorinated organics (includes 1 low salinity test material)	Seawater
31 & 33	AQ-6	2	Volatile organochlorines	Seawater
31 & 33	AQ-7	2	Pentachlorophenol	Seawater
31 & 33	AQ-8	3	Triazines & organophosphorus organics (includes 1 low salinity test material)	Seawater
<b>SEDIMENTS</b>				
30 & 32	MS-1	2	Trace metals (includes 1 wet sediment in Round 32)	Silty sediment
30 & 32	MS-2	2	Chlorinated organics (includes 1 wet sediment in Round 32)	Silty sediment
30 & 32	MS-3	2	PAHs	Silty sediment
<b>BIOTA - Stabilised wet biological tissue</b>				
30 & 32	BT-1	2	Trace metals	Fish & shellfish
30 & 32	BT-2	2	Chlorinated organics	Fish & shellfish
32	BT-3	2	Non <i>ortho</i> CBs, PCDDs and PCDFs	Fish & shellfish
30	BT-4	2	PAHs	Shellfish
32	BT-5	3	Chlorobornanes (toxaphene)	Wet tissues & fish oil
32	BT-6	2	Trace metals	Fucus
33	BE-1	2 species	Imposex in marine snails	Marine snails
<b>DEVELOPMENT EXERCISES</b>				
33	DE-3	3	Organotins in biota	Solution & shellfish
33	DE-5	3	Organotins in seawater	Solution & seawater
33	DE-6	3	Chlorophyll <i>a</i>	Filtered test materials
33	DE-7	3	Organotins in sediment	Solution & sediment
33	DE-8	3	Brominated flame retardants	Solution & biota

**Appendix 6.1 Percentages of determinand/matrix combinations that were categorised as acceptable by the data filter – shown by laboratory.**

Lab. Code	Nutrients	Met sed	PCB Sed	PAH sed	Met bio	PCB bio	Ocl bio	Pah bio
A	67	100	-	100	78	100	50	-
B	100	-	90	77	63	52	21	53
C	100	67	100	-	89	-	-	-
D	83	100	100	100	-	100	-	100
E	83	100	-	-	-	-	-	-
F	100	100	-	-	100	100	79	90
G	67	92	100	97	100	100	48	-
H	-	-	86	90	-	-	-	-
I	100	100	100	100	89	100	-	50

**Notes**

1. Determinand matrix classes in top row of table – Nutrients, metals in sediment, polychlorinated biphenyls in sediment, polycyclic aromatic hydrocarbons in sediment, metals in biota, polychlorinated biphenyls in biota organochlorine compounds in biota, polynuclear aromatic hydrocarbons in biota
2. The data filter acceptance criterion is a score of greater than 45 (40 for trace organic determinands). The values in the table show the percentage of determinand matrix combinations in each class that achieved this acceptance level. For example, the nutrients class comprises 6 determinands, so a given laboratory will have 6 opportunities to pass or fail in each of three years, that is a total of 18 possible passes. If 6 of these are failures the % acceptance is 67%. For each individual failure the associated data would not be classified as acceptable.
3. The colour coding merely shows different bands of pass rates 0-50 brown, 50-75 yellow and 75-100 green.
4. A dash indicates that data for the determinand class are not provided by the laboratory

## Appendix 6.2 Summary Proficiency Test data for core NMMP determinands

Lab. Code	Nutrients	Met sed	Oclsed	PAH sed	Met bio	Ocl bio	PAH bio
A	87	94	81	52	10	59	58
B	70	96	69	47	87	37	43
C	45	92	68	-	64	49	-
D	94	66	84	96	59	52	94
E	98	93	32	-	-	-	-
F	85	73	-	-	56	33	25
G	94	73	60	71	75	45	57
H	-	-	29	38	-	20	23
I	93	96	62	73	74	43	61

For assessment of data quality on the basis of proficiency tests the pass criterion for each test is that the laboratory “z score” (a standardised measure of its error) should be less than 2. The values in the table represents the percentage of pt test analyses carried out over 3 years (usually 6-12) that meet this criterion.

The green colours show the determinand matrix combinations that would have been deemed acceptable on the basis that a 50% pass demonstrates fitness for purpose.

## Appendix 6.3

### Detailed Proficiency Test data for NMMP determinands - metals and trace organochlorines in seawater – assessed for fitness for purpose on the basis of proficiency test performance alone

The green colours show the determinand matrix combinations that were deemed acceptable on the basis that a 50% pass rate demonstrates fitness for purpose.

Lab. Code	B	C	E	F	I
Arsenic	100	100	-	91	100
Boron	-	-	64	67	83
Cadmium	91	82	-	64	71
Chromium	88	100	-	-	80
Copper	55	82	100	100	93
Iron	-	-	-	-	-
Lead	82	82	64	86	79
Manganese	-	-	-	-	-
Mercury	83	88	17	40	67
Nickel	100	100	79	86	100
Silver	-	-	-	-	7
1,2,3-TCB	100	100	33	91	-
1,2,4-TCB	63	83	100	91	-
Vanadium	88	100	33	91	-
3,3'-TCB	-	-	-	3	100
a-HCH	-	88	33	78	-
b-HCH	-	100	33	67	-
d-HCH	-	-	-	56	-
Dieldrin	88	86	67	55	-
Endosulphan-I	60	50	-	75	-
Endosulphan-II	-	-	33	100	-
g-HCH	75	100	67	67	-
HCB	75	43	67	91	-
HCBD	-	80	-	82	-
op'-DDT	-	50	67	45	-
PCP	88	88	100	100	-
pp'-DDD	38	100	33	64	-
pp'-DDE	75	100	67	73	-
pp'-DDT	50	57	67	73	-
Trifluralin	88	100	100	73	-

## Appendix 6.4 Example of data filter scores for year 2000

### Nutrients in water and determinands in sediment

	ammonia	nitrite	nitrate	SRP	Silicate	chloro	Al	Cd	Hg	Cu	Pb	Ni	Zn	As	Cr	Li	Fe
A	40	73	80	81	82	23	74	76	59	74	83	68	83	76	74	69	81
B	60	64	80	81	62	57	0	0	0	0	0	0	0	0	0	0	0
C	46	63	73	60	74	58	0	86	30	93	88	95	98	93	65	0	0
D	90	70	83	72	82	10	73	75	48	88	86	75	90	76	65	63	58
E	93	87	87	87	90	10	79	72	66	80	79	61	85	71	66	67	72
F	85	77	87	77	90	67	87	75	88	97	82	85	83	93	77	82	90
G	26	75	75	71	72	15	72	61	80	80	76	81	83	68	73	25	75
H																	
I	89	89	92	83	92	67	92	83	78	87	82	93	97	97	97	85	87

	cb28	cb52	cb101	cb118	cb138	cb153	cb180	nap	phen	anth	pyr	baa	chry	bap	bpy	ipy	flu
A								74	59	62	62	41	59	49	54	54	62
B	54	57	63	68	73	73	64	38	64	55	49	58	58	76	73	63	61
C	77	70	67	74	67	67	64	0	0	0	0	0	0	0	0	0	0
D	63	43	49	62	56	56	59	63	60	63	63	51	60	67	67	64	68
E	7	12	10	10	13	10	7	0	0	0	0	0	0	0	0	0	0
F	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
G	73	66	61	71	65	71	61	52	70	85	73	65	80	73	73	73	73
H	41	45	48	50	53	45	33	29	47	45	46	48	47	54	50	52	46
I	57	58	75	61	74	56	46	57	83	79	79	76	79	84	83	72	79



### Determinands in biota

	Cd	Cu	Pb	Ni	Zn	As	Cr	Ag	Hg	pcb28	pcb52	pcb101	pcb118	pcb138	pcb153	pcb180
A	64	70	55	35	73	60	36	54	70	71	61	76	79	83	86	79
B	40	37	35	40	45	0	45	15	45	30	40	57	38	43	62	48
C	70	65	55	77	82	78	65	0	78	17	0	0	0	0	0	0
D	15	30	15	0	30	7	0	0	0	65	54	56	67	67	70	78
E																
F	63	75	49	61	85	71	55	84	80	55	51	62	66	67	63	71
G	67	75	52	66	72	53	66	57	58	50	47	57	47	49	52	60
H																
I	75	76	63	48	80	83	65	27	50	54	55	53	58	45	50	41

	ahch	bhch	ghch	dhch	opddt	ppddt	pptde	ppdde	diel	ald	end	isod	hcb	hcbd
A	71	15	69	0	15	56	61	76	66	0	0	0	71	0
B	20	20	20	20	20	38	47	44	59	20	20	20	38	5
C	0	0	0	0	0	0	0	0	0	0	0	0	0	0
D	0	0	22	0	0	7	15	30	0	0	0	0	7	0
F	47	48	40	46	82	50	61	74	67	50	39	45	49	33
G	43	39	37	0	60	29	28	42	27	30	33	33	50	25
H														
I	8	8	8	8	13	36	31	37	20	8	8	8	20	8

	nap	phen	anth	pyr	baa	chry	bap	bpy	ipy	flu
A	7.5	15.0	15.0	7.5	15.0	30.0	7.5	30.0	30.0	22.5
B	37.0	52.5	34.5	67.0	27.0	49.5	27.0	42.0	17.0	67.0
C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
D	50.0	65.0	60.0	67.0	60.0	70.0	60.0	60.0	60.0	65.0
F	29.0	47.0	47.0	76.0	46.0	76.0	46.0	46.0	41.0	46.0



## **APPENDIX 7. LABORATORY IMPROVEMENT PLANS**

### **7.1. EHS (formerly IRTU)**

#### **1. PCBs in Sediment.**

The analytical procedure has been updated to include:

- Improved alumina cleanup to achieve lower reporting limits and reduce uncertainty at lower concentrations.
- Revalidation of the performance of the method.
- The use of CRM(s) certified for the full range of CB congeners determined.
- An LRM or CRM is included with each batch of analyses

#### **2. Li, Mn and Fe in Sediment**

- Li, Mn and Fe will be added to the scope of accreditation.
- QC for all determinands are covered by the new CRM (MESS – 3).
- QC charts are kept for all determinands using the CRM results.
- Performance in QUASIMEME is satisfactory (>75%)

#### **3. Nutrients in Seawater**

Testing of analytical systems

- A low range QC sample has been introduced.
- Within batch random error will be estimated i.e. two concentrations per chemistry @ 12 observations each.

This will be carried out for our 5 existing QC's plus the 5 new QC's (all in  $\mu\text{M/L}$ ):

#### **4. Chlorophyll a**

- Certified standards are purchased to calibrate the fluorometer.
- The new Turner TD700 will be performance tested prior to use.

- A stable solid secondary AQC sample has been purchased and is used as a system suitability check.
- The instrument is recalibrated regularly.
- Control charts are plotted for the secondary AQC samples.

While these steps can be instigated for any chosen method, the difficulty in chlorophyll <sub>a</sub> analysis remains the extraction of the compound from the algae found at the sample site. Until a standard method for freshwater and /or marine samples is agreed then consistency across the different laboratories will remain patchy. Improvements will be made with the introduction of AQC but a great deal of advice will be necessary from those laboratories that have already implemented suitable procedures for Quality control, to those that have yet to start.

## 7.2 DARDNI

### ORGANIC DETERMINANDS

#### PCB in Sediment

1. Validation of the method using Accelerated Solvent Extraction (ASE) has been carried out using CRM536. Methodology is currently being extended to sample analysis.
2. Material has been collected and is being prepared for an in-house Laboratory Reference Material (LRM)
3. The present QC involves analysis of CRM 536 with each batch of samples. Once sufficient data has been obtained for the new LRM this will be used as a second QC with each batch to provide QC at two different concentration levels. This will provide data in order to calculate both between batch and within batch variation.

#### PAH in Sediment

1. Current extraction procedure (Soxhlet) to be replaced by ASE which will be validated when it has been established as an extraction method.
2. An in-house LRM to be prepared.
3. Current QC involves analysis of HS 6 with each batch of samples. Once sufficient data has been obtained for the new LRM this will be used as a second QC sample. As with PCB's this will provide data to calculate both between batch and within batch variation.

#### OCR/PCB in Shellfish

1. ASE has replaced Soxhlet extraction
2. Clean-up procedure has been improved to enable reporting limits to be lowered in line with NMMP (Green Book ) requirements.
3. Method validation has been carried out.
4. An in-house LRM to be prepared.
5. At present the QC involves analysis of a spiked sample with each batch of samples. Once sufficient data has been obtained for the new LRM this would be used as a second QC. As before this will provide data at two concentration levels in order calculate both within batch and between batch variation.

#### PAH in Shellfish

1. New procedure has been established using ASE.
2. Problems: No CRM's available
3. An in-house LRM has been prepared

## **NUTRIENT DETERMINANDS**

### **Determination of Ammoniacal Nitrogen in Seawater**

1. A standard ammonia solution obtained from Ocean Scientific is now used routinely as an independent QC material.
2. Fresh solutions will be prepared at intervals and the analysis data obtained presented on QC charts.

## **CHLOROPHYLL DETERMINATION**

### **Fluorometric Determination of Chlorophyll-a in Seawater**

1. No stable reference material.
2. Replicate samples are being used to provide information on the precision of the procedure and a control chart established using this data.
3. The accuracy of the fluorometric procedure is being monitored by comparing results with similar samples analysed using Lorenzen's monochromatographic method.

## **METAL DETERMINANDS**

### **Sediment**

1. A procedure for Lithium has yet to be established.
3. Re-validation for Mn has been carried out.
4. Limits of Detection (LOD) to be improved in line with NMMP (Green Book) targets

### **Shellfish**

1. A satisfactory procedure for Selenium has been established.
2. Limits of Detection (LOD) to be improved in line with NMMP (Green Book) targets.

## **SUPPORTING DETERMINANDS**

Total Lipid  
Method received UKAS accreditation

Moisture  
Method received UKAS accreditation.

## 7.3 Environment Agency

### National Laboratory Service Improvement Plans.

The National Laboratory Service carries out NMMP work at 4 laboratories. Most of the improvements centre around standardising on a best practice for all the laboratories. This will help in the NLS gaining group accreditation for our sediment and biota methods.

The use of CRMs and procedural QC controls are standard practice in the NLS for this analysis.

- **PCBs and PAHs in sediment**

The methodologies used across the NLS for the analyses are broadly similar. The aim is to standardise on a 'best practice'.

Both PCB and PAH analyses contribute significant blanks during the prep process. By standardising our methods the aim is to control the blank impact.

The PCB method needs revalidating, as the recovery against the CRM is poor.

- **Metals in sediment and biota**

The methodologies used across the NLS for the analysis are to be standardised on micro-wave digestion followed by ICP-MS. Micro-wave digestion reduces the blank levels considerably from 'open' digestion techniques.

- **Nutrients in Seawater**

The NLS uses standard methodologies for these determinands. There is a move to reduce the number of sites carrying out this work to improve laboratory efficiencies.

External QC and Internal QC checks are carried out for this analysis. There is a need to investigate the performance of the method around the level of detection on a routine basis.

- **Chlorophyll a**

The method used at some NLS sites uses UV detection. Our technical work groups are evaluating the 'best practice'. The likelihood is fluorescence will be the preferred detection method.

Currently, all our sites filter the sample onto the same pore-sized filter. However, the organic extraction step before UV detection is different across our sites.

### Additional Work

- Ultra low level OCPs in seawater

- Improvements in the GC-MS analysis of the Drins and HCHs in biota which are subject to considerable mass ion interference. (Using NCI for example.)
- Analysis of various OPs in seawater.



## **7.4 SEPA (East) Improvement Plans**

### **PAH in sediments and biota**

The methods have been performance tested using QUASIMEME validated material. Recovery is poor and the cause of this is being investigated. Extraction using ASE is also being developed and will be validated prior to analysis of samples.

### **Trace Metals in Biota**

Extraction is being revalidated for a new temperature and pressure controlled microwave oven. Analyses are being transferred to ICP/MS. The changes require revalidation of the method.

### **Organochlorines in sediments and biota**

Sample extraction is being transferred to ASE and will require full validation before it is adopted for routine use.

### **Nutrients**

The methods have been performance tested and meet the required criteria. Silicate results have a slight negative bias which needs investigating.

### **Chlorophyll**

The method is accredited and performance tested. The instrument is calibrated annually using a certified reference material. Freeze dried spinach and a solid secondary standard are used as routine QC checks.

### **TBT**

Method development for TBT in sediments has been suspended due to lack of resources. It is hoped that staff time will be made available later in the year for method development. SEPA East have subscribed to the QUASIMEME development exercises for TBT in sediments, biota and waters.

## 7.5 SEPA (West) Improvement Plans

### Trace Metals in Water

The method for trace metals in saline waters employs matrix modification prior to quantification by ICP-MS, and is UKAS accredited. Excellent results have been obtained in Quasimeme laboratory performance scheme (LPS) exercises. The method has recently been amended to include system suitability checks prior to quantification by ICP-MS, to ensure that the instrument is free of contamination and that the required sensitivity is obtained for low level samples.

### Mercury in Water

The method is UKAS accredited, and excellent results have consistently been achieved in Quasimeme LPS exercises. Despite this, to continually improve our methods, a new automated mercury analyser has been purchased to allow measurement by fluorescence, which allows lower limits of detection than the previous absorption technique.

### Nutrients in Seawater

SEPA West routinely analyses all its nutrients samples, including those from Quasimeme LPS exercises, on board the Survey Vessel Endrick II. A five-channel autoanalyser has been used since 2000, and the methods are UKAS accredited. The procedures have been steadily improved with time, in conjunction with the instrument supplier Bran and Luebbe. For example, to provide more stable baselines and better sensitivity, the light sources in the colorimeters have been replaced with light emitting diodes (LEDs). Consistently good results have been obtained in Quasimeme LPS exercises for nitrate, nitrite, phosphate and silicate. However, results for ammonia were consistently poor, and an improvement plan was set in place to try to rectify the situation. Several changes were made to the procedure, including the introduction of a new low calibration range for coastal water samples and more extensive use of low nutrient seawater for all standards and calibrants. These changes have proved successful, with z-scores of 0.40 and 0.56 for the seawater samples, and 0.62 and 1.65 for the estuary water samples in Quasimeme Round 30 in 2002.

## **7.6 LABORATORY IMPROVEMENT PLAN FOR FRS**

### **1. CBs in sediment and biota.**

FRS's extraction procedure for CBs in sediment and biota will hopefully be investigated this year. Currently Soxhlet extractions are used. However, an Accelerated Solvent Extractor (ASE) will be purchased this year and new methods will be developed using this procedure. All CB methods will have to be re-validated using the new extraction procedure.

The purity of solid CB standards used for the preparation of the calibration standards will be investigated. Where necessary the final concentrations in calibration standards will be amended to reflect the purity.

### **2. Nutrients in Seawater**

The new Bran & Luebbe CFA purchased for the analysis of nutrients both at sea and in the lab has now been validated and methods are UKAS accredited. Extensive investigations both in the lab and at sea demonstrated that limits of detection were lower and precision better than the previous system. However, this work also highlighted that fluctuations in the laboratory temperature may cause problems, particularly for the analysis of silicate. An air conditioning system will be purchased this year for the nutrient laboratory to improve the measurement of nutrients.

The FRS programme for 2003-04 requires an investigation into the storage of seawater samples for nutrient analysis, with the aim of finding the best storage method for all nutrients. A report on this work is required by March 2004.

### **3. PAHs in sediment**

Similar to the CBs methods the extraction of sediments for PAHs using ASE will be investigated. The current sediment methods use sonication. Sediment samples will be analysed using both extraction procedures and comparisons made. If the ASE extraction procedure is found to be suitable the PAH methods will be re-validated using the amended methods.

### **4. Trace Metals in sediment and biota**

The agreed FRS programme for SEERAD for 2003 - 04 includes improvements to the analysis of total concentrations of metals in sediment by ICP-MS. The main areas of investigation, where it is suspected that significant improvement may be possible, are:

- HF digestion conditions and duration
- Influence of digest matrix on instrument response
- Matrix matching of standard solutions to samples.

A report on this work is due in March 2004.

## **5. TBT in sediment**

Method development in this area will continue as part of FRS's programme for 2003-04. Previous work using sodium borohydride as a derivatising agent to produce the hydride derivatives was found to be unsatisfactory. A number of problems were encountered with the hydrides, stability of the standards and reproducibility being the main difficulties. An alternative derivatisation is the formation of alkyl derivatives, such as ethyl derivatives. Commercially available ethyl derivatives were analysed by GC-MSD and results looked promising. Therefore future method development will concentrate on the preparation of ethyl derivatives for analysis by GC.

## 7.8 CEFAS Laboratory Improvement Plans

### Nutrients

1. We are aiming towards gaining UKAS accreditation for the determination of nitrite, total oxidized nitrogen, phosphate, silicate and ammonia. In order to gain accreditation the following laboratory steps have been identified as being necessary together with the generation of the required documentation:
  - Conduct thorough tests on the new Skalar autoanalyser to fully quantify limits of detection and quantification, precision, accuracy (ie. carry out thorough method validation).
  - Purchase Certified Reference Materials for nutrients in seawater as soon as they become commercially available later this year. At present there are no such solutions commercially available and currently we buy high concentration nutrient solutions in DI water and make the appropriate dilutions in seawater. These unknowns are run as Performance Evaluation standards. However, this necessary dilution is already a potential source of error before analysis of the PE standard.
  - Ensure that all low nutrient seawater (LNSW) we collect for the preparation of standards and dilution of samples is filtered to 0.2  $\mu\text{m}$ .

### Chlorophyll:

- A new Turner fluorometer was bought and has not yet been commissioned. This gives a direct digital readout of chlorophyll concentration. The current fluorometer gives a readout on a dial and therefore this introduces operator error in determining the reading. The availability, cost and potential use of a chlorophyll CRM is to be investigated.

### Metals

### Sediments

Data from Quasimeme indicate the performance is good. Improvements over the past years have included Arsenic, Mercury and Cadmium. Cadmium does still present a problem at low concentrations this is made more difficult by the high boric acid matrix used for the neutralisation of the HF. In the medium term the problem is likely to be overcome by the use of collision cell technology with ICP-MS to be purchased soon. This should allow use of the more sensitive Cd114 isotope. The results indicate that the analytical methodology works. The major problem is in maintaining consistency, particularly with ever changing turnover staff. Improvements identified are therefore to improve the SOP's and protocols along with on the job training.

## Biota

Improvements have particularly been seen in Mercury and Lead in recent years. Chromium remains a specific problem with a molecular isobaric overlap at Cr52 giving false high concentrations. Again this problem should be overcome by the new collision cell technology. Arsenic has always had a positive bias; although z scores have been maintained within +2 over the years, again this problem is due to isobaric overlap in the ICP-MS technique on As75. This problem can also be overcome by the new technology to be incorporated soon.

### Organohalogen work area

There are a number of areas that we are currently addressing during the calendar year.

1. The first is to improve the percentage of acceptable Quasimeme Z scores for the determination of OCP's in sediment and biota with an initial target of 80%  $Z \leq 2$  during the first year.
2. Improve sample throughput by reducing reliance on manual methods.
3. Improve cost effectiveness by introduction more on-line sample preparation.
4. Achieve UKAS accreditation to ISO17025 during FY 2003/4
5. Increase on line data capture and reduce reliance on manual data transcription to reduce error rate.
6. Review use of CRM's and LRM's.

In common with a number of NMMP laboratories our worst group of determinands are OCP's in biota and sediments and we are taking active steps to improve this performance. The generic poor performance can be related to a number of issues identified by a step by step approach.

- Concentrations of OCP's have largely declined in both sediments and biota. Non detects are common and with the use of gas chromatography – electron capture detection (GC-ECD) the risk of false positives rises.
- Clean-up techniques that were suitable when concentrations were higher are now under more pressure to remove larger amounts of matrix co-extractives as the concentrations of target compounds decrease.
- On-column degradation of e.g. pp'DDT can be more of an issue at lower concentrations.
- Few low (if any) level CRM's are available.

We will address these issues by :-

- Investigate the more routine use of gas chromatography – mass spectrometry (GC-MS) phasing out, as funds permit, the reliance on GC-ECD. Low resolution MS in EI mode is unlikely to offer the required detection limits in selected ion monitoring mode with either a quadrupole or an ion trap instrument. However GC-MS in the negative ion chemical ionisation mode is comparable in sensitivity to ECD and has been shown to give reliable data in routine use cf. the routine

determination of brominated flame retardants.

- Although the use of gravity fed alumina and silica adsorption columns are robust and relatively cheap (in terms of materials) the associated staff costs are high, QA/QC overhead and the generally limited capacity for lipids also begins to restrict their use. With the greater reliability of high performance gel permeation (HRGPC) columns and the impact of modern automated and integrated LC systems we have invested and are currently in the process of validating a new HRGPC methodology using cyclohexane and ethyl acetate as mobile phases thus also avoiding the more common use of chlorinated solvents for GPC. The new system will have a much greater capacity for lipid removal allowing for an improvement in detection limits or conversely a greater degree of sample clean-up for a similar sample mass
- The use of HRGPC can be coupled with on-line silica fraction on the same instrument for further fractionation and final lipid removal if required, this is currently under investigation
- As well as giving some considerable attention to our sample clean-up and fractionation we are also moving away from traditional Soxhlet extraction systems to microwave assisted solvent extraction (MASE). The newer system have numerous advantages over Soxhlet systems including faster extraction times, lower solvent consumption and a reduction in the laboratory foot print and the need for the work to be undertaken in a fume cupboard. We are currently investigation the use of cyclohexane/ethyl acetate solvent mixtures to replace n-hexane/acetone. This will have the advantages of being able to undertake the extraction in a GPC friendly solvent and avoid a manual solvent change step.
- As a general principle all NMMP analytical methodology will be accredited to ISO17025 during the current financial year.
- We are undertaking an audit of data handling procedures to reduce the risk of transcription errors and provide a more robust archival system. Likely actions are an increase in the level of on-line data capture and transfer to our LIMS system.
- We are auditing our use of CRM's and LRM's to ensure that our RM's more closely match our common matrices and expected concentration levels

## **PAH work area**

As part of the laboratory improvement plan CEFAS are currently modifying the PAH extraction method from a reflux style alkaline saponification to a microwave assisted alkyl saponification extraction, new primary standards are being prepared and the number of deuterated internal standards used for quantification is being increased. Therefore the methods will be re-optimised following these improvements and the future QUASIMEME results scrutinised for signs of improvement.

## Appendix 8.1

**QUASIMEME Workshop on the Analysis of Chlorophyll *a* in Seawater at  
MUMM,  
Royal Belgian Institute for Natural Sciences  
Oostende  
1<sup>st</sup> to 2<sup>nd</sup> July 2002**

Attended by 27 people, representing 9 European countries.

### Presentations

- Role of Chlorophyll *a* in assessing eutrophication status
- HPLC measurements of phytoplankton pigments
- *In situ* Fluorimetric measurements of Chlorophyll *a*
- Overview of the QUASIMEME Laboratory Performance Studies with reference to applying a standard method
  
- Sampling and Analysis for Chlorophyll *a*
- Remote sensing and modelling

**Group Discussion:** the problems and solutions for the measurement of pigments in seawater

### Plenary Discussions

- Technical discussion of the last interlaboratory study
- Summary of the Workshop, review of the Wishing Wall and the design of the next QUASIMEME Laboratory Performance for Chlorophyll *a*

Laboratory demonstrations and Manufacturers demonstrations

### Posters

- The Determination of Chlorophyll *a* and Phaeophytin using the Turner TD-700 Fluorometer
  
- Determination of chlorophyll *a* and *b* and phaeophytine *a* and *b* concentration in surface waters (salinity 18-35) with HPLC
  
- QUASIMEME: An Holistic Model for Quality Measurement in the Marine Environment



## Appendix 8.2

**QUASIMEME Workshop on the Analysis of Organotin Compounds in Marine  
Matrices  
at  
Institute of Environmental Studies,  
Free University  
Amsterdam  
3<sup>th</sup> to 5<sup>th</sup> July 2002**

Attended by 45 people, representing 11 countries world-wide.

### **Presentations**

- Organotin determinations in sediment
- Overview of Organotin Analysis what has happened, where we are, where we are going.
- Recent Developments in the IVM method: Accelerated Solvent Extraction and Isotope Dilution
- The analysis of organotins in sediment and mussels. Method used by RIKZ.
- Calibration, Recovery Corrections and the use of CRMs
- ICP.MS methods
- Sample handling for organotin analysis. Be prepared!
- Effects of halogen element in Grignard reagent and tropolone on propylation of organotins
- Risk analysis in OT-SAFE
- Evaluation of the QUASIMEME Laboratory Performance Studies for Organotin compounds in marine matrices

### **Plenary discussions**

- Why do we need a workshop? Organotins are easy to measure.
- Discussion reports from the group discussions and plenary discussion and recommendations for methods and techniques used for organotin analysis
- The way forward. The requirements for the QUASIMEME Laboratory Performance Studies.

### **Group discussions**

- Is correction for recovery necessary? For and Against Accelerated Solvent Extraction; Do we need Tropolone?
- Organotin standards and calibrants; Ethylation v Propylation

Tour of the laboratories at IVM and specific demonstrations

### **Posters**

- Effects of halogen element in Grignard reagent and tropolone on propylation of organotins

- Organotin Speciation Analyses in Marine Biota using NaBEt<sub>4</sub> Ethylation and GC-FPD
- Determination of organotin compounds
- QUASIMEME: An Holistic Model for Quality Measurement in the Marine Environment