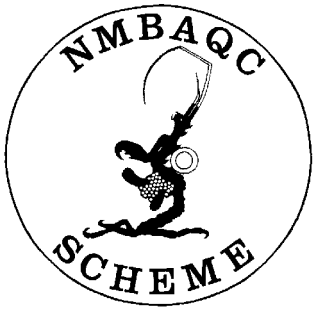

The National Marine Biological Analytical Quality Control Scheme

Particle Size Analysis Component Report from the Contractor Scheme Operation – Year 16 2009/10

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August 2010

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PARTICLE SIZE ANALYSIS COMPONENT REPORT FROM THE CONTRACTOR

SCHEME OPERATION – YEAR 16 – 2009/10

Linked Documents (hyperlinked in this report)

Particle Size Results – PS34

Particle Size Results – PS35

Description of the Scheme Standards for the Particle Size Analysis Component

1. Introduction

The National Marine Biological Analytical Quality Control (NMBAQC) Scheme addresses three main areas relating to benthic biological data collection:

- The processing of macrobenthic samples.
- The identification of macrofauna.
- The determination of physical parameters of sediments.

The sixteenth year of the Scheme (2009/10) followed the format of the fifteenth year. A series of exercises involved the distribution of test materials to participating laboratories and the centralised examination of returned data and samples. The labelling and distribution procedures employed previously have been maintained and specific details can be found in the Scheme's annual reports for 1994/95 and 1995/96 (Unicomarine, 1995 & 1996).

Twelve laboratories participated in the particle size analysis component of the Year 16 NMBAQC Scheme; six were government laboratories; six were private consultancies. Half of the participants (6) were responsible for CSEMP (Clean Seas Environment Monitoring Programme) sample analysis. To reduce potential errors and simplify administration, LabCodes were assigned in a single series for all laboratories participating in the benthic invertebrates, fish and particle size components of the NMBAQC Scheme (due to Unicomarine administering these three components).

As in previous years, some laboratories elected to be involved in limited aspects of the Scheme. CSEMP laboratories were required to participate in all relevant components of the Scheme, although this was not strictly enforced.

1.1 Summary of Performance

This report presents the findings of the Particle Size Analysis components for the sixteenth year of operation of the National Marine Biological Analytical Quality Control (NMBAQC) Scheme.

This component consisted of one module with two exercises:

- Analysis of two sediment samples for physical description (Particle Size module).

The analytical procedures of this module were the same as for the fifteenth year of the Scheme. The results for the two exercises are presented and discussed. Comments are provided on the performance for each of the participating laboratories in each of the exercises.

The **Particle Size exercises (PS)** were conducted as in the previous Scheme year. 'Pass/fail' criteria were applied based upon z-scores from the major derived statistics with an acceptable range of ±2 standard deviations (see Description of the Scheme Standards for the Particle Size Analysis Component). The influence of in-house methodologies on the results returned for the PS34 exercise was minimal in the two sets of *replicate* results produced by the benchmark laboratories; this is partly attributable to the use of only Malvern laser instruments and some standardised protocols, *i.e.* no use of chemical dispersants or hydrogen-peroxide pre-treatment. In most cases there was reasonably good agreement between participant laboratories for both PS exercises. The first particle size exercise of the Scheme year (PS34; sandy mud sample) received eleven data returns that resulted in five 'fail' and fifty 'pass' flags; two of these fails are the result of a transcription / spreadsheet errors. The second particle size exercise of the Scheme year (PS35; slightly gravelly muddy sand sample) received eleven data returns that resulted in ten 'fail' and forty-five 'pass' flags; six of these fails were produced by three of the five participants that did not record a gravel component in their results.

Comments are provided on the individual performance of the participating laboratories in each of the above components. A summary of their performance with respect to standards determined for the CSEMP is presented.

1.1.1.1 Statement of Performance

Each participating laboratory received a 'Statement of Performance', which included a summary of results for each of the Schemes modules and details the resulting flags where appropriate. These statements were first circulated with the 1998/1999 annual report, for the purpose of providing proof of Scheme participation and for ease of comparing year on year progress.

2. Summary of PSA Component

2.1 Introduction

There is one module in the particle size component; Particle Size Analysis (PS) module.

This module is described in more detail below. A brief outline of the information to be obtained from the module is given, together with a description of the preparation of the necessary materials and brief details of the processing instructions given to each of the participating laboratories.

2.1.1 Logistics

The labelling and distribution procedures employed previously have been maintained and specific details can be found in the Scheme's annual reports for 1994/95 and 1995/96 (Unicomarine, 1995 & 1996). Email was the primary means of communication for all participating laboratories. This has considerably reduced the amount of paper required for the administration of the Scheme.

2.1.2 Data returns

Return of data to Unicomarine Ltd. followed the same process as in previous years. Spreadsheet based forms (tailored to the receiving laboratory) were distributed for each circulation via email, with additional hard copies where appropriate. All returned data have been converted to Excel 2003 format for storage and analysis. In this and previous Scheme years slow or missing returns for exercises lead to delays in processing the data and resulted in difficulties with reporting and rapid feedback of results to laboratories. Reminders were distributed shortly before each exercise deadline.

2.1.3 Confidentiality

To preserve the confidentiality of participating laboratories, each are identified by a four-digit Laboratory Code. In September 2009 each participant was given a confidential, randomly assigned Scheme year sixteen LabCode. Codes are prefixed with the Scheme year to reduce the possibility of obsolete codes being used inadvertently by laboratories, *e.g.* Laboratory number four in Scheme year sixteen will be recorded as LB1604.

In the present report all references to Laboratory Codes are the post-August 2009 codes (Scheme year sixteen), unless otherwise stated. To further reduce potential errors and simplify administration, LabCodes were assigned in a single series for all laboratories participating in the benthic invertebrates, fish and particle size analysis components of the NMBAQC Scheme (due to Unicomarine administering these three components).

2.2 Particle Size Analysis (**PS**) Module

2.2.1 Description

This component examined the production of derived statistics from the particle size analysis of replicate sediment samples. Two samples of sediment, one fine the other coarser (PS34 and PS35), were distributed in 2009/10. The set of PS34 of replicate samples were derived from natural marine sediments; PS35 replicates were artificially prepared from components of both natural sediment and commercial aggregate materials; they were prepared as described below. In each case a random subsample of the prepared replicates were divided for laser diffraction analysis using two differing instruments at separate laboratories to ensure sample replicate consistency and illustrate any potential variations between the laser instruments. For both PS34 and PS35 the *replicates* were analysed using Malvern Mastersizer 2000 and Malvern Mastersizer X instruments to produce benchmark data.

2.2.1.1 Preparation of the Samples

One of the PS circulations sediment was collected from a natural marine environment (Harwich for PS34); the other was artificially created from both natural and commercially acquired materials (PS35). Natural material was returned to the laboratory and coarse sieved (1 mm) to remove gravel, shell and large faunal content. A minimum of 30 litres of visually similar sediment was collected. Following sieving, the sediment for PS circulation was well mixed in a large tray and allowed to settle for a week. The sediment was sub-sampled by coring in pairs. One core of a pair was stored as the 'A' component, the other as the 'B'. To ensure sufficient weight for analysis, and to further reduce variation between distributed PS samples, this process was repeated three times for each sample *replicate, i.e.* each distributed sample was a composite of three cores. The artificial PS replicates were produced by combining known quantities of homogenised material; for PS35 quantities of mud, sand and gravel were included.

The numbering of the replicate samples was random. All of the odd-numbered 'B' components (a total of 14) were sent for particle size analysis to assess the degree of inter-sample variation and produce benchmark data. For both PS34 and PS35, half the *replicates* were analysed using a Malvern Mastersizer 2000 laser and half by a Malvern Mastersizer X log bed laser. The 'A' components were assigned to participating laboratories randomly and distributed according to the Scheme timetable.

2.2.1.2 Analysis required

The participating laboratories were required to conduct particle size analysis on the samples using their normal technique (either in-house or using a subcontractor) and to return basic statistics on the sample including %< 63µm, mean, median, sorting and skewness. A written description of the sediment characteristics was to be recorded (pre-processing and post-processing using the Folk Triangle) along with an indication of any peroxide treatment. Also requested was a breakdown of the particle size distribution of the sediment, to be expressed as a weight of sediment in half-phi (ϕ) intervals. Approximately **nine weeks** were allowed for the analysis of each PS sample (PS34 and PS35).

2.2.2 Results

2.2.2.1 General comments

Twelve laboratories subscribed to the exercises in 2009/10. One of the laboratories did not submit returns for either of the exercises; this is indicated in the tables by a dash (-).

Most participating laboratories now provide data in the requested format, though some variations remain. As previously reported, it should be remembered that the results presented may be from a more limited number of analytical laboratories than is immediately apparent since this component of the Scheme is often sub-contracted by participants to one of a limited number of specialist laboratories. For PS34, eleven out of twelve participating laboratories returned data; one laboratory did not provide data or provide notification of abstention. For PS35, eleven out of twelve participating laboratories returned data; one laboratory did not provide data or provided notification of abstention. Detailed results for each exercise have been reported to the participating laboratories (PS34 and PS35); additional comments are added below.

2.2.2.2 Analysis of sample replicates (benchmark data)

Replicate samples of the sediment used for the two PS distributions were analysed using two different laser diffraction instruments to examine *replicate* and instrument variability and establish benchmark data. *Replicates* have been examined by both laser and sieve / pipette methods in earlier Scheme years; however as the majority of laboratories are conducting analyses by laser diffraction the testing of *replicates* is now undertaken using two different laser instruments. For PS34 and PS35, half the *replicates* were analysed using a Malvern Mastersizer 2000 laser and half by a Malvern Mastersizer X log bed laser. *Replicate* analyses were performed by Plymouth University, Geography Department (Malvern Mastersizer 2000) and Martin Ryan Marine Science Institute (Malvern Mastersizer X, log bed). Some minor methodology differences were noted between the data sets supplied by the two laser instruments; however the *replicate* samples analysed by each instrument showed very good agreement.

Sample PS34 comprised sandy mud sediment (average of 50.89% <63µm). The Malvern Mastersizer X results showed very good agreement, with only slight scatter in the very fine sand to medium silt categories between the PS34 *replicate* samples; the Malvern Mastersizer 2000 showed no discernable variation between *replicate* samples. As with previous PS circulations, the distribution curves produced by each instrument differed, however the divergence was minimal. The minimised variance could potentially be due to the common pre-treatment and dispersant methodology followed by the two laser instruments. The slight divergence of *replicates* illustrated by the Mastersizer X results is likely to have been influenced by low number of subsample replicates analysed to produce the data set for each sample, *i.e.* natural variation within each PS sample has not been adequately 'averaged'. Results for the individual *replicates* are provided in Table 1 and are displayed in Figure 1 (PS34 Report).

Sample PS35 comprised an artificial mixed sediment (slightly gravelly sand; average of 6.54% <63µm). The Malvern Mastersizer X results showed good agreement between the PS35 *replicate* samples; the Malvern Mastersizer 2000 showed very good agreement between *replicate* samples. As with the PS34 results, slight methodology differences were noted between the data sets supplied by the two laser instruments. Differing cumulative distribution curves were once again produced by the two instruments (Malvern Mastersizer 2000 and Malvern Mastersizer X). The divergence of replicates illustrated by the Mastersizer X results is likely, as in PS34, to have been influenced by low number of subsample replicates analysed to produce the data set for each sample. The Mastersizer 2000 instrument produced an average silt/clay content figure of 8.32%; this figure was 4.76% for the Mastersizer X data. Results for the individual *replicates* are provided in Table 1 and are displayed in Figure 1 (PS35 Report).

2.2.2.3 Results from participating laboratories

Summary statistics for the two PS circulations are presented in Table 1 in each individual exercise report (see PS34 Report and PS35 Report). After resolution of the differences in data format, the size distribution curves for each of the sediment samples were plotted and are presented in Figures 2 in each individual exercise report (see PS34 and PS35). Included in each of these Figures, for comparison, are the mean distribution curves for the *replicate* samples as obtained by Unicomarine Ltd. (using Malvern Mastersizer X and Mastersizer X instruments), Figure 3 (PS34) and Figure 4 (PS35) in the exercise reports show the z-scores for each of the derived statistics. The z-scores were calculated with outliers and replicated data removed from the mean estimations of each of the major derived statistics.

2.2.2.3.1 Thirty-fourth distribution – PS34

There was generally good agreement for PS34 between the results from the analysis of *replicates* and those from the majority of participating laboratories (see Figure 2). One laboratory (LB1603) pre-treated their replicate with hydrogen peroxide; this is likely to be accountable for their high % silt / clay value (68.6%) and the displacement of their cumulative curve. One laboratory (LB1604) provided a figure for Inclusive Graphic Skewness that was not mathematically possible and did not reflect their raw data; this was subsequently attributed to a spreadsheet error. All of the participants used the laser diffraction technique to analyse the sample. Two participants (LB1604 and LB1606) conducted sieve analysis down to 63µm and utilised laser diffraction for just the silt/clay fraction, these laboratories produced very similar, distinctive cumulative curves. Table 1 shows the variation in data received from the participating laboratories. The derived statistic for %silt/clay ranged from 45.76% to 68.6%, excluding data from the *replicate* analyses produced by Unicomarine Ltd.

2.2.2.3.2 Thirty-fifth distribution – PS35

There was generally good agreement for PS35 between the results from the analysis of *replicates* and those from the majority of participating laboratories (see Figure 2). Five laboratories (LB1602, LB1604, LB1605, LB1620, and LB1623) did not record gravel content in their results. Five of the participants used a combination of sieving and laser diffraction to analyse the sample; five participants stated that they used laser diffraction only; and one participant dry sieved their entire sample. Table 1 shows the variation in data received from the participating laboratories. The derived statistic for %silt/clay ranged from 2.6% to 19.36%, excluding data from the *replicate* analyses produced by Unicomarine Ltd.

2.2.3 Discussion

The difference between the laser instruments employed for particle size *replicate* analysis (Malvern Mastersizer X and Malvern Mastersizer 2000) was minimal and agreement within each benchmark data set was very good.

The samples distributed as PS34 appeared from an analysis of *replicates* (Figure 1) to be good replicates with very little variance within the two sub-sets of samples (Malvern Mastersizer 2000 and Malvern Mastersizer X). Results from participating laboratories (Figure 2) showed a general similarity in distribution curves, except for that of LB1603; this was the only laboratory to pre-treat the sample with hydrogen peroxide, which resulted in a %silt/clay value 15.72% higher than the average. NMBAQC Scheme standard PSA methods are being devised to minimise the potentially significant variances in PSA data observed due to differing pre-treatments. Figure 3 shows the z-scores for each of the major statistics supplied by the participating laboratories. Two laboratories (LB1604 and LB1623), despite producing a relatively typical cumulative curve, supplied erroneous data for their sample's Inclusive Graphic Skewness and mean particle size, respectively.

The samples distributed as PS35 appeared from an analysis of *replicates* (Figure 1) to be good replicates with little variance within the two sub-sets of samples (Malvern Mastersizer 2000 and Malvern Mastersizer X). Results from participating laboratories were relatively well grouped (Figure 2). Five of the participating laboratories (LB1604, LB1605, LB1620, LB1623 and LB1627) stated that they used only laser diffraction to analyse their replicate samples (one of these records, LB1627, appears to be incorrect as >2mm data has been provided); these laboratories have presumably decided to ignore the small gravel content supplied in their artificial replicates. One laboratory (LB1602) failed to record a gravel component despite analysing the sample using sieves and laser diffraction; this appears not to be an omission due to policy as zeros are entered in their data sheet. Figure 4 shows the z-scores for each of the major statistics supplied by the participating laboratories.

Participating laboratories were asked to provide a visual description of the PS34 and PS35 samples prior to analysis. The results were variable and some were extremely descriptive (Table 1, final column, in PS34 and PS35). Participating laboratories were also instructed to describe the sediment using the Folk triangle after analysis. Data were provided by all eleven participating laboratories for both PS34 and PS35. Eight of the eleven laboratories, that submitted data using the Folk triangle, described PS34 as 'Sandy mud' (x 6) or 'Sandy silt' (x 2); two recorded 'Muddy sand'; and one recorded 'Silt'. Three of the eleven laboratories, that submitted data using the Folk triangle, described PS35 as '(g)mS' / 'Slightly gravelly muddy sand' or 'Slightly shelly, silty sands'; two recorded 'Slightly gravelly sand'; two recorded 'Medium sand'; two recorded 'Muddy sand'; and two laboratories recorded 'Sand'.

It is essential that analytical methods, including pre-treatment, are stated when reporting or attempting to compare results. The situation is further complicated by the fact that the difference between the techniques and the effects of the pre-treatment also varies with the nature of the sediment sample. As demonstrated in these and previous PS exercises, possible variations in equipment and methods can result in highly variable data. In order to eliminate as much variation as possible a detailed and prescriptive method for particle size analysis is being devised for the CSEMP sample analysis.

2.2.4 Application of NMBAQC Scheme Standards

One of the key roles of the Particle Size Analysis component of the NMBAQC Scheme is to assess the reliability of data collected as part of the Clean Seas Environment Monitoring Programme (CSEMP; formerly UK NMMP). With this aim performance target standards were defined for certain Scheme modules and applied in Scheme year three (1996/97). These standards were the subject of a review in 2001 (Unicomarine, 2001) and were altered in Scheme year eight; each performance standard is described in detail in the Description of the Scheme Standards for the Particle Size Analysis Component document. Laboratories meeting or exceeding the required standard for a given exercise would be considered to have performed satisfactorily for that particular exercise. A flag indicating a 'Pass' or 'Fail' would be assigned to each laboratory for each of the exercises concerned. It should be noted that, as in previous years, only the Scheme's OS and PS exercise have been used in 'flagging' for the purposes of assessing data for the CSEMP. As the Scheme progresses, additional exercises may be included. In the meantime, the remaining modules and exercises of the Scheme are considered of value as more general indicators of laboratory performance, or as training exercises.

If a participant failed to return results for the PS module it resulted in the assignment of a "Fail" flag to the laboratory for each pass / fail assessment. The only exception to this approach has been in those instances where laboratories elected not to participate in a particular exercise.

2.2.4.1 Laboratory Performance

The z-scores and results in each of the two PS exercises are presented in Table 2 and Figure 3 in the PS34 and PS35 Reports. The assigned flags for each laboratory for each derived statistic are also given. Where no returns were made for an exercise this is indicated in the tables with a "-".

Application of the new PS exercise standards, introduced in Scheme year nine, (see Description of the Scheme Standards for the Particle Size Analysis Component) is shown in the PS34 and PS35 Particle Size Results reports (see Table 2 and Figure 3 in the PS34 Report and Table 2 and Figure 4 in the PS35 Report).

Table 2 shows the results for the PS34 exercise. One laboratory (LB1611) is deemed to have failed all criteria due to non-submission of data. One participating laboratory (LB1603) failed to meet the standard for %< 63µm; all participating laboratories passed the median (ϕ) and sorting standards; one laboratory (LB1623) failed the standard for mean (ϕ); three laboratories (LB1603, LB1604 and LB1623) failed to meet the standard for IGS (SKi). Eight of the eleven participating laboratories passed all standards (LB1601, LB1602, LB1605, LB1606, LB1620, LB1625, LB1627 and LB1635).

Table 2 shows the results for the PS35 exercise. One laboratory (LB1611) is deemed to have failed all criteria due to non-submission of data. Two participating laboratories (LB1602 and LB1635) failed to meet the standard for %< 63µm; two laboratories (LB1602 and LB1603) failed the standard for median (ϕ); three laboratories (LB1602, LB1603 and LB1620) failed to meet the standard for mean (ϕ); one laboratory (LB1625) failed to meet the standard for sorting; two laboratories (LB1602 and LB1623) failed to meet the standard for IGS (SKi). Six of the eleven participating laboratories passed all standards (LB1601, LB1604, LB1605, LB1606, LB1625 and LB1627).

3. Conclusions and Recommendations

A number of observations may be made from the results of the exercises described above. The following is a summary of the major points of importance.

1. Laboratories should endeavour to report their PS results in the requested format, *e.g.* at half phi intervals. This would enable the direct comparison of data from all participants and simplify the creation of cumulative curve figures. Participants should review their data prior to submission; several PS failures have been the direct result of faulty spreadsheet formulae and straightforward transcription errors. Zeros should only appear in submitted data where no material was present; dashes, '- ', should appear where analysis has not been conducted.
2. Laboratories involved in CSEMP data submission should endeavour to return data on **ALL** necessary components of the Scheme in the format requested. This will be required to allow the setting of performance "flags". Non-return of data will result in assignment of a "Fail" flag. For CSEMP laboratories this deemed "Fail" for no submitted data is to be perceived as far worse than a participatory "Fail" flag.
3. Particle size exercises (PS) over the past sixteen years have shown differences in the results obtained by different techniques (laser and sieve / pipette), in-house methods (*e.g.* pre-treatment) and also differences between equipment (*e.g.* Malvern Mastersizer 2000, Mastersizer X and Coulter LS230 lasers). PS data indicates that the variance between laser and sieve results is further emphasised by certain sediments characteristics. The overall range of these variances needs to be determined if combining data sets derived from differing methods. It is essential that particle size data should be presented with a clear description of the method of analysis and equipment used.
4. PS exercises have highlighted the need for a prescriptive method for laser analysis (including equipment specifications) for the analysis of CSEMP samples. Replicate samples analysed using the same broad technique can result in highly variable summary statistics. A particle size standard operating procedure is to be developed through the NMBAQC Scheme for the CSEMP. The final draft will accommodate consultation and feedback from all significant parties and should be available for Scheme Year 17 (2010/11).
5. An improved learning structure to the Scheme through detailed individual exercise reports has been successfully implemented and was continued in this Scheme year. For the PS exercises, detailed results have been forwarded to each participating laboratory as soon after the exercise deadlines as

practicable. Participants that submit significantly incorrect data are contacted immediately to ensure that in-house checks can be implemented to ensure future quality assurance. The PS34 and PS35 reports included the data submission sheets received from all participants as an appendix; the PS35 report included an additional figure to display the proportions of each major particulate grouping recorded by each laboratory; this revised reporting structure will be continued for all future PS reports. Participants are encouraged to review their exercise reports and provide feedback concerning content and format wherever appropriate.

6. Accurate representation of PS circulated samples using laser analysis can only be achieved via analysing multiple subsamples of the material. Several subsamples should be prepared from the bulk sample and these in turn analysed several times by laser diffraction. The final PSA results should be an average of these analyses.

7. The current NMBAQC Scheme standards for PSA are under review. The use of z-scores is inappropriate for such a low number of data returns where two erroneous results can significantly alter the pass / fail criteria. The z-score method also assumes that the majority of respondents are correct and raised genuine concerns regarding technique and method bias. Alternative flagging criteria will be trialled for use in Scheme Year 17 (2010/11).

4. References

Folk, R.L. (1974) *The Petrology of Sedimentary Rocks.* Hemphill Publishing Co. Texas

Hall, D.J. (2009) *National Marine Biological Analytical Quality Control Scheme. Particle Size Results: PS34.* Report to the NMBAQC Scheme participants. Unicomarine Report NMBAQCps34, October 2009.

Hall, D.J. (2010) *National Marine Biological Analytical Quality Control Scheme. Particle Size Results: PS35.* Report to the NMBAQC Scheme participants. Unicomarine Report NMBAQCps35, February 2010.

Hall, D.J. (2010) *National Marine Biological Analytical Quality Control Scheme. Description of Scheme Standards for the Particle Size Analysis Component from Scheme Year 8 (2001/02) to Year 16 (2009/10).* Report to the NMBAQC Scheme participants. Unicomarine report NMBAQCpsa_stds, February 2010.

Unicomarine (1995) *National Marine Biological Quality Control Scheme. Annual Report (Year one).* Report to the NMBAQC Committee and Scheme participants. September 1995.

Unicomarine (1996) *National Marine Biological Quality Control Scheme. Annual Report (Year two).* Report to the NMBAQC Committee and Scheme participants. September 1996.

Unicomarine (2001) *National Marine Biological Analytical Quality Control Scheme. Own Sample Format and Standards Review: Current Problems and Proposed Solutions.* Report to the NMBAQC Committee. April 2001.