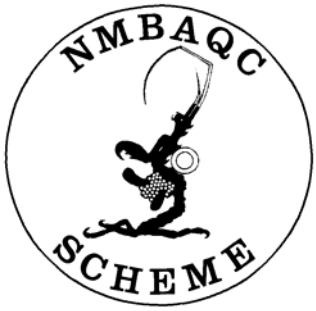

The National Marine Biological Analytical Quality Control Scheme

Particle Size Analysis Component Report from the Contractor Scheme Operation – Year 14 2007/08

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PARTICLE SIZE ANALYSIS COMPONENT REPORT FROM THE CONTRACTOR

SCHEME OPERATION – YEAR 14 – 2007/08

Linked Documents (hyperlinked in this report)

Particle Size Results – PS30

Particle Size Results – PS31

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 fourteenth year of the Scheme (2007/08) followed the format of the thirteenth 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 NMBAQC Scheme (including one laboratory utilising replicated data). Seven laboratories were government laboratories; five were private consultancies. Over half of the participants (7) were responsible for CSEMP (Clean Seas Environment Monitoring Programme) sample analysis.

As in previous years, some laboratories elected to be involved in limited aspects of the Scheme. CSEMP laboratories were required to participate in all 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 fourteenth 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 modules were the same as for the thirteenth 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 pre-treatment and the use of chemical dispersants on the results returned for the PS30 exercise was clearly evident. In most cases there was reasonably good agreement between laboratories for both exercises. The first particle size exercise of the Scheme year (PS30; muddy sand sample) received eleven data returns (including replicated data) that resulted in seven 'fail' and forty-eight 'pass' flags. The second particle size exercise of the Scheme year (PS31; gravelly sand sample) received eleven data returns (including replicated data) that resulted in eight 'fail' and forty-seven 'pass' flags.

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 has received a 'Statement of Performance', which includes 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. Each Scheme year fourteen participant was given a confidential LabCode in September 2007, these codes were randomly assigned. These 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 fourteen will be recorded as LB1404.

In this report all references to Laboratory Codes are the post-August 2007 codes (Scheme year fourteen), unless otherwise stated. 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).

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 coarse the other much finer, were distributed in 2007/08. The first set of replicate samples, PS30, was derived from natural marine sediments; the second, PS31, was artificially created; both were prepared as described below. In each case a random subsample of the prepared replicates were divided for laser diffraction analysis using either a Malvern laser (Mastersizer X) or a Coulter laser (LS230) to ensure sample replicate consistency and illustrate any potential variations between these two laser instruments.

2.2.1.1 Preparation of the Samples

For the PS30 circulation sediment was collected from a natural marine environment. This material was returned to the laboratory and coarse sieved (1 mm) to remove gravel, shell and large faunal content. For PS31 aggregate material was sourced to artificially create a set of replicates to purposefully test the blending of sieve and laser derived data. A minimum of 30 litres of visually similar sediment was collected for each circulation. Following sieving, the sediment for each PS circulation was well mixed in a large tray and allowed to settle for a week. Each 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 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. Half the replicates were analysed using Malvern laser and half by a Coulter 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. **Eight weeks** were allowed for the analysis of the first PS sample (PS30) and **seven weeks** were allowed for the second PS sample (PS31).

2.2.2 Results

2.2.2.1 General comments

The exercises in 2007/08 were undertaken by twelve laboratories. 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 are for 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 PS30, eleven out of twelve participating laboratories returned data (including laboratories with grouped results); one laboratory did not provide data or provide notification of abstention. For PS31, eleven out of the 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 (PS30 and PS31); additional comments are added below.

2.2.2.2 Analysis of sample replicates

Replicate samples of the sediment used for the two PS distributions were analysed using two different laser diffraction instruments. *Replicates* have previously been examined by both laser and sieve/ pipette methods, however as the majority of laboratories are conducting analyses by laser diffraction the testing of *replicates* is now undertaken using two different laser instruments. Half of the *replicates* were analysed using the Malvern Mastersizer X laser and half by the Coulter LS230 laser. *Replicate* analyses were performed by Plymouth University, Geography Department (Malvern) and Partrac (Coulter).

Some clearly significant methodology differences were noted between the data sets supplied by the two laser instruments, however the seven PS30 *replicate* samples analysed by each instrument showed very good agreement. There was very good agreement between the *replicate* samples analysed using the Malvern Mastersizer X laser; the Coulter LS230 laser results showed slightly more variability (see Figure 1 in PS30 Report). Both instruments produced data to classify the PS30 *replicate* samples as muddy sand samples. The shape of the cumulative distribution curves differed between the two laser instruments; this divergence is likely to be the result of pre-treament with hydrogen peroxide and the use of a chemical dispersant (sodium hexametaphosphate) by the Malvern laser laboratory. The figures for %<63µm varied significantly between the two instruments with the Malvern instrument producing an average figure of 31.52% and the Coulter 22.27%. Consequently, the derived statistics were slightly different between the two instruments. Results for the individual *replicates* are provided in Table 1 and are displayed in Figure 1 (PS30 Report).

Sample PS31 was of an artificially created gravelly sand sediment (average of 5.01% <63µm). The Coulter results showed slight variation between the PS31 *replicate* samples; the Malvern showed

practically no variation between *replicate* samples. As with the PS30 results, potentially significant 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 X and Coulter LS230). The Malvern instrument produced an average silt/clay content figure of 1.56%; this figure was 8.47% for the Coulter data. The Malvern derived data displayed approximately 5% more gravel content than that of the Coulter. Results for the individual *replicates* are provided in Table 1 and are displayed in Figure 1 (PS31 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 PS30 Report and PS31 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 PS30 and PS31). Included in each of these Figures, for comparison, are the mean distribution curves for the *replicate* samples as obtained by Unicomarine Ltd. (using Malvern and Coulter instruments), Figure 3 in the individual 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.

One laboratory, which normally sub-contract their particle size analysis to another laboratory (also participating), elected to utilise the results from this laboratory for PS30 and PS31; this laboratory's data are regarded as replicated data and are not included in the calculation of z-scores. This laboratory is indicated in the report Tables by an asterisk against their LabCode. Accordingly the results from the sub-contracting laboratory have been used in the Figures and Tables as appropriate. In Figures 2 and 3 (PS30 and PS31) only data from the sub-contracting laboratory are displayed, although it also applies to the contracting laboratory. For Table 1 in each report, which present the summary statistics, although the results are displayed for all participating laboratories the replicated data supplied by the centralised laboratory (sub-contractor) have been included only once in the calculation of mean values for each exercise. Performance flags (as discussed in Section 2.2.4: Application of NMBAQC Scheme standards) have been assigned to laboratories using replicated data in the same manner as for other laboratories.

2.2.2.3.1 Thirtieth distribution – PS30

There was generally good agreement for PS30 between the results from the analysis of *replicates* and those from the majority of participating laboratories, with the exception of the higher silt / clay fraction recorded by the Malvern *replicates* (see 2.2.2.2 Analysis of sample replicates). The cumulative curve (Figure 2) for one laboratory (LB1410) was notably atypical due to a virtual absence of particles larger than very fine sand. One laboratory (LB1422) recorded a figure of -1.22 for sorting, which was opposed to the majority of results and was not reflected in their raw data. All of the participants used the laser diffraction technique to analyse the sample. Table 1 shows the variation in data received from the participating laboratories. The derived statistic for %silt/clay ranged from 7.6% to 26.7%, with all laboratories producing figures lower than the combined *replicate* analyses produced by Unicomarine Ltd.

2.2.2.3.2 Thirty-first distribution – PS31

There was generally good agreement for PS31 between the results from the analysis of *replicates* and those from the majority of participating laboratories for the proportion of the sample finer than medium sand. However, major differences were noted in results for the coarse fraction of the PS31 sample (see Figure 2). The results from LB1401 and LB1402 were notable atypical as they provided no gravel proportion in their raw data. All except two of the participants used a combination of dry sieving and laser diffraction to analyse the sample; LB1402 used only laser diffraction and LB1415 used only dry sieving analysis methods. Table 1 shows the variation in data received from the participating laboratories. The derived statistic for %silt/clay ranged from 0.6% to 4.9%, with all the participating laboratories producing figures lower than the *replicate* analyses average figure produced by Unicomarine Ltd.

2.2.3 Discussion

The difference between the two laser instruments employed for particle size *replicate* analysis (Malvern Mastersizer X and Coulter LS230) was evident, however the differences observed in PS30 and PS31 are

likely to have been more influenced by the differing in-house analysis methods (hydrogen peroxide pre-treatment to remove organic material and use of sodium hexametaphosphate as a chemical dispersant to separate) than laser instrumentation. NMBAQC Scheme standard methods are to be devised to minimise the potentially significant difference in PSA data observed by pre-treatment.

The sample distributed as PS30 appeared from an analysis of *replicates* (Figure 1) to be very uniform and the results from participating laboratories (Figure 2) were relatively closely grouped, with the exception of one data set. Figure 3 shows the z-scores for each of the major statistics supplied by the participating laboratories. Data received from one laboratory (LB1410) indicated practically no material less than 3.5phi (greater than very fine sand), hence this set of results are clearly atypical in the cumulative curve figure (Figure 2). One laboratory (LB1422), despite producing a relatively typical cumulative curve, supplied erroneous data for the sample's sorting co-efficient that is likely to the result of either a transcription or calculation error.

The samples distributed as PS31 appeared from an analysis of *replicates* (Figure 1) to be good replicates with little variance within the two sub-sets of samples (Malvern and Coulter). Results from participating laboratories were particularly poorly grouped for gravel and coarse sand content (Figure 2). PS31 was the first PS circulation to purposefully contain a gravel component and was designed to test the capability of participants to deal with such samples. Laboratories that routine use laser diffraction for material smaller than 2mm needed to use sieve analysis for the greater than 2mm fraction and subsequently merge these data. Consequently the large variety of results received for PS31 could be the result of any of the stages of this 'double processing'. Two laboratories did not provide raw data for the gravel component; however, one of these laboratories included 'gravel' in their description of the sediment. The omission of this gravel component would render the derived statistics incomparable, because several of the statistics require the measurement of the 95% percentile of the whole sample. Some laboratories did not decipher the 95% percentile and yet still submitted full, unqualified, statistics for PS31. Transcription errors were observed (LB1408, mean phi) along with an error associated with some Malvern software producing reversed – or + results for skewness (LB1401). The full range of possible data were received for skewness, with laboratories recording coarse tails, fine tails and normal distributions of particles. The same was true for the sorting co-efficient, data received ranged from moderately well sorted to very poorly sorted. Figure 3 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 PS30 and PS31 samples prior to analysis. The results varied considerably and some were extremely descriptive (Table 1, final column, in PS30 and PS31). Participating laboratories were also instructed to describe the sediment using the Folk triangle after analysis. Data were provided by nine laboratories for PS30 and nine laboratories for PS31. Six of the nine laboratories, that submitted data using the Folk triangle, described PS30 as 'Muddy sand'; two recorded 'Sand'; and one described 'Poorly sorted very fine sand'. Six of the nine laboratories, that submitted data using the Folk triangle, described PS31 as 'Gravelly Sand'; three recorded 'Sand'; and one laboratory recorded 'Poorly sorted fine sand'.

It is essential that analytical methods, including pre-treatment, are stated when reporting or attempting to compare results. The situation is complicated further 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 must be 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 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 PS30 and PS31 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 PS30 and PS31 Particle Size Results reports (see Table 2 and Figure 3 in the PS30 and PS31 Reports). Table 2 shows the results for the PS30 exercise. One laboratory (LB1407) is deemed to have failed all criteria due to non-submission of data. One laboratory (LB1415) failed to meet the standard for %< 63µm; four laboratories (LB1402, LB1405, LB1406 and LB1410) failed the standard for median (ϕ); all laboratories passed the standard for mean (ϕ); one laboratory (LB1422) failed to meet the standard for sorting; and one laboratory (LB1404) failed to meet the standard for IGS (SKi). Four of the eleven participating laboratories passed all standards (LB1401, LB1403, LB1408 and LB1423).

Table 2 shows the results for the PS31 exercise. One laboratory (LB1407) is deemed to have failed all criteria due to non-submission of data. One laboratory (LB1401) failed to meet the standard for %< 63µm; two laboratories (LB1406 and LB1410) failed the standard for median (ϕ); one laboratory (LB1408) failed to meet the standard for mean (ϕ); three laboratories (LB1402, LB1405 and LB1422) failed to meet the standard for sorting; one laboratory (LB1408) failed to meet the standard for IGS (SKi). Four of the eleven participating laboratories passed all standards (LB1403, LB1404, LB1415 and LB1423).

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.
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. The Scheme's particle size exercises (PS) 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 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.

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. 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 need to be reviewed. 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.

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