NMBAQC

NE Atlantic Marine Biological Analytical Quality Control Scheme

Particle Size Analysis Component Annual Report
Scheme Operation 2017/2018 (Year 24)

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PARTICLE SIZE COMPONENT ANNUAL REPORT FROM APEM Ltd

SCHEME OPERATION – 2017/18 (Year 24)

NMBAQC

NE Atlantic Marine Biological Analytical Quality Control Scheme

Linked Documents (hyperlinked in this report):

Particle Size Exercise Results – PS64

Particle Size Exercise Results – PS65

Particle Size Exercise Results – PS66

Particle Size Exercise Results – PS67

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1. Introduction

The NE Atlantic 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 and the determination of physical parameters of sediments.

APEM Ltd has been the administrative contractor for the Particle Size component since 2014 (Scheme year 21).

The particle size component of the scheme comprises of two modules:

- The PS Ring Test (PS).
- The PS – Own Sample (PS-OS).

The PS module followed the same format of 2016/17; a series of exercises involved the distribution of test materials to participating laboratories and the centralised examination of returned data and samples.

The PS-OS module, introduced in the 2014/15 Scheme year, followed the same logistical format as the previous year. Selected participant samples are re-analysed by the NMBAQC Scheme PSA contractor and the results are compared. The Particle Size Own Sample module is a training / audit module and the purpose of this module is to examine the accuracy of particle size analysis for participants' in-house samples.

Sixteen laboratories signed up to participate in the 2017/18 PS module exercises (PS64, PS65, PS66 and PS67); seven were government laboratories and nine were private consultancies. Thirteen laboratories signed up to participate in the PS-OS module exercises (PS-OS10, PS-OS11 and PS-OS12); eight were government laboratories and five were private consultancies. One government laboratory had two Lab Codes to submit six PS-OS samples for AQC analysis.

To reduce potential errors and simplify administration, Lab Codes were assigned with a prefix to determine the Scheme component; all codes for the Particle Size component were prefixed with "PSA_".

As in previous years, some laboratories elected to be involved in limited aspects of the Scheme. Competent monitoring authorities (CMAs) completing PSA in support of biological analysis for monitoring programmes (including in assessment of MPA (Marine Protected Areas), as evidence under MSFD (Marine strategy framework directive) and WFD (Water framework directive), as well as the CSEMP (Clean Seas Environmental Monitoring programme), must participate in this component of the Scheme. The Scheme is aware of other PSA methodologies (*e.g*. those used in the Regional Seabed Monitoring Plan) and encourages those involved in any relevant PSA monitoring programmes to participate in this Scheme, especially where pass/fail criteria can be used to assess overlapping aspects of different methodologies.

1.1 Assessing Performance

For 2017/18 (Scheme year 24) both the PS and PS-OS reports will follow a similar format with each sample analysis section broken down for review, including sieve processing, laser processing, data merging and summary statistics. Laboratories will then receive a “Good” or “Review” flag based on their results; “Review” flags will have accompanying comments as to where mistakes have been made and how to correct them.

1.2 Statement of Performance

Each participating laboratory received a copy of the interim results for each exercise; these included a summary of results provided by each laboratory and a basic discussion of any major outliers. Further details and analysis can be found in this report.

At the end of the Scheme year each laboratory received a ‘Statement of Performance’ certificate, which included a summary of results for each of the Scheme’s 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

The two 2017/18 year PSA modules, PS and PS-OS are 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.

2.2 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.

2.3 Data returns

Spread-sheet based workbooks were distributed to each participating laboratory via email for each circulation and data returned to APEM Ltd via the NMBAQC Scheme email address. 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.

2.4 Confidentiality

To preserve the confidentiality of participating laboratories, each was identified by a four-digit Laboratory Code prefixed with "PSA_", to identify the scheme component. In May 2017 each participant was given a confidential, randomly assigned 2017/18 (Scheme year twenty-four) Lab Code. Codes are prefixed with the Scheme year to reduce the possibility of obsolete codes being used inadvertently by laboratories, *e.g.* Laboratory number twelve in Scheme year twenty-four (2017/18) was recorded as PSA_2412.

3. Particle Size Analysis (PS) Module

3.1 Description

This component examined the percentage of sediment found in each half-phi interval from the particle size analysis of replicate sediment samples. Four samples of sediment, one fine (PS64), one coarser (PS67) and two mixed (PS65 and PS66) were distributed in 2017/18. The samples were distributed in two stages; the first circulation (PS64 and PS65) was sent to participants on 10th July 2017 and the second circulation (PS66 and PS67) was sent on the 13th October 2017. For each circulation participants were given approximately 6 weeks to complete their analysis and send completed workbooks via email to APEM Ltd. PS64 and PS66 replicate samples were derived from natural marine sediments; PS65 and PS67 replicates were prepared from a combination of natural sediments and artificially prepared commercial aggregate; they were prepared at APEM's Letchworth laboratory as described below.

3.1.1 Preparation of the Samples

The first PS circulation, PS64, was a mud collected from natural marine environments at Gweek Quay, Helford River. Approximately 20 litres of visually similar sediment was collected and returned to the laboratory where it was wet sieved at 0.5mm to remove any particles larger than 0.5mm. Sediment that passed through the 0.5mm sieve was retained in a large tray, mixed and left to settle, any excess water was removed before it was cored into replicate samples approximately 200 grams in weight. The second exercise, PS65, was a mixed sample created from known amounts of commercially acquired pea shingle (split into half-phi intervals by dry sieving using a mechanical sieve shaker) with known quantities of sand from the Eastbourne coast, East Sussex. The sand was pre-sieved through a 1mm sieve to remove any larger particles before being mixed and left to dry out. The third exercise sample (PS66) was a diamicton sample made from natural sediments consisting of a mixture of gravel (>1mm) from the River Wandle, a tributary of the Thames, pre-sieved (<1.0mm) sand from near the Cutty Sark at Greenwich, Thames estuary, and a pre-sieved (<0.5mm) mud from Gweek Quay, Cornwall. The gravel was c wet sieved through a 1mm sieve in the laboratory to remove sediment less than 1mm; the greater than 1mm sediment was then dried and split into half-phi fractions using a mechanical sieve shaker. The final sediment (PS67) was created using natural offshore sediments containing shell fragments from the South East Coast and commercially acquired pea shingle split into half-phi intervals by dry sieving using a mechanical sieve shaker. For the mixed samples (PS65 and PS66) approximately 250g of water was added to help mix the sample together.

Five replicates from each of these exercises were sent to Kenneth Pye Associates Ltd (KPAL) for particle size analysis to assess the degree of inter-sample variation and produce benchmark data. Where laser diffraction analysis was required, these replicates were analysed using a Coulter LS13320 laser diffraction instrument. The remaining replicates were randomly assigned to participating laboratories and distributed according to the Scheme timetable. Spare replicates were kept at the APEM Ltd. Letchworth laboratory in case of problems such as damaged samples during delivery or significant processing errors.

3.1.2 Analysis required

The participating laboratories were required to conduct particle size analysis on the samples following the NMBAQC Scheme's best practice guidance for particle size analysis to support biological data (NMBAQC Best Practice Guidelines (Mason, 2016)), either in-house or using a subcontractor. A summary of the sample as a written description of the sediment characteristics was to be recorded, with a qualitative visual assessment made prior to -processing, using the Folk (1954) textural classification. In addition, the percentages of gravel, sand and silt/clay and any use of peroxide treatment or chemical dispersant were to be noted. Also requested was a breakdown of the particle size distribution, expressed as a weight or volume percentage at half-phi (ϕ) intervals, for each of the raw sieve data (>1mm), the raw laser data (<1mm) and the final merged data set.

The 2017/18 workbooks had the same format as the previous year. Data provided in the "Participant Sieve Metadata" and "Participant Laser Metadata" spreadsheet tabs were for analytical purposes only and were not published in the Interim Results reports. This year the Benchmark metadata have been included as appendices in each sample report for participants to see how the Benchmark Lab analysed each sample.

Approximately six weeks were allowed for the analysis of each pair of PS samples sent out (i.e. PS64 & PS65, PS66 & PS67).

3.2 Results

3.2.1 General comments

Sixteen laboratories subscribed to the exercises in 2017/18. For the first circulation (PS64 and PS65) all subscribing participants provided results; for the second circulation (PS66 and PS67) all but one participant provided results. PSA_2409 did not participate in exercise PS66 and PSA_2415 did not participate in exercise PS67; both provided email confirmation of their non-participation.

Most participating laboratories now provide data in the requested format, although some variations remain. As reported previously, 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. Detailed results for each exercise (PS64, PS65, PS66 and PS67) have been reported to the participating laboratories; additional comments are provided below.

3.2.2 Analysis of sample replicates (Benchmark Data)

Five replicate samples of the sediment used for the four PS distributions were analysed by KPAL to examine variability and establish benchmark data that participant results can be compared with. Replicate samples supplied by APEM were analysed, where required, using

Endecotts British Standard 300mm and 200mm test sieves, Endecotts EFL 2000/2 and Retsch AS2001 Control 'g' sieve shakers and a Beckman Coulter LS13320 laser size analyser. In previous Scheme years replicates were analysed by both laser diffraction and sieve / pipette methods; however, as the majority of laboratories are now conducting analyses by laser diffraction the testing of replicates for 2017/18 was undertaken only using a laser diffraction instrument.

The analysis results for the benchmark replicates were assessed by APEM to analyse the variability between the replicates and to establish the reproducibility of the samples. The analysis showed an overview of the sample including percentage Gravel, Sand and Mud along with a description of the sediment using the textural group from a Gradistat output of the final data e.g. Slightly Gravelly Muddy Sand. The processing of the sample was split into sieve and laser analysis. Sieve analysis is displayed in a table with the raw weight recorded in each half phi interval from -6.5 to 0.0phi and the weight of the less than 1mm oven dried sample plus any sediment from the base pan of the sieve shaker. In the PS66 and PS67 reports the percentage weight in each half-phi category is also displayed graphically in a bar chart for visual comparison.

Laser analysis included a table of the final laser data for each replicate along with a graph showing the differential and cumulative percentage. The triplicate analysis undertaken to obtain the final laser data was presented as graphs in the report for PS66.and in a table for PS64 and PS65. For each replicate sample the Coefficient of Variation (CV) was calculated for the D_{10}, D_{50} and D_{90} particle size in microns. The CV is most commonly expressed as the standard deviation as a percentage of the mean and describes the dispersion of a variable in a way that does not depend on the variables' measurement units. A low CV indicates a smaller amount of dispersion in the variable. Good laser reproducibility was shown for replicates when the %CV was <3% for the D_{50} and <5% for the D_{10} and D_{90}, all limits were doubled when the D_{50} was less than 10µm, in line with recommendations in BS ISO 13320.

Benchmark analysis of the replicates for Sample PS64 indicated an average composition of 0.01% gravel, 22.32% sand and 77.66% mud, classified as "Slightly Gravelly Sandy Mud" according to the Blott & Pye (2012) scheme. Despite these samples being pre-sieved through a 0.5mm sieve, small weights (on average 0.058g) of sediment greater than 1mm were found. This reflects variability in the efficiency with which elongate particles, mainly shell fragments, pass through a given sieve size. Analysis of the triplicate laser analysis for each replicate sample showed that the %CVs for the D_{10}, D_{50} andD_{90} were well within the acceptable limits and therefore the replicates were deemed to have good reproducibility. Results for the individual replicates are provided in Tables 1, 2, 3 and 4 and are displayed in Figures 1 and 2 in the PS64 Report.

Sample PS65 was a mixed sediment and contained an average of 50.26% gravel, 48.79% sand and 0.95% mud, classified as a 'Sandy Gravel' according to the Blott & Pye (2012) scheme. The replicates were analysed by dry sieving and laser analysis. The sieve data shows consistent results between the replicates and triplicate laser analysis showed extremely low variation, with %CV well below acceptable levels for each statistic. Results for the individual replicates are provided in Tables 1, 2, 3 and 4 and are displayed in Figures 1 and 2 in the PS65 Report.

Sample PS66 was a diamicton and both sieve and laser analyses were required. The sample contained an average of 8.39% gravel, 66.89% sand and 24.72% mud and was classified as Gravelly Muddy Sand' according to the Blott & Pye (2012) scheme. Sieve analysis showed slight variation between the replicates; Replicate 5 was the only replicate to record sediment (4.92g) in the interval -4.5 to -4.0 (one gravel particle retained on the 16mm sieve) and Replicate 2 recorded a slightly lower weight than the other replicates in interval -3.5 to -3.0 (retained on the 8mm sieve). The overall weight of sediment greater than 1mm and less than 1mm was consistent across all the replicates. These variations were taken into consideration when assessing participant results. The laser triplicate analysis showed extremely low variation, with %CV well below the acceptable levels for each statistic. Results for the individual replicates are provided in Tables 1, 2, 3 and 4 and are displayed in Figures 1 and 2 in the PS66 Report.

Sample PS67 was a gravel sample and only required sieve analysis. The results showed an average of 84.72% gravel and 15.28% sand. The sediment is classified as 'Gravel' according to the Blott & Pye (2012) scheme. The benchmark lab commented that due to the large amounts of gravel in the sample it was impossible to take a representative sub-sample for laser analysis. Therefore the entire sample (> 1 mm and < 1mm fractions) was sieved at half phi intervals and the data entered into the merged data sheet. Results for the individual replicates are provided in Tables 1, 2, 3 and 4 and are displayed in Figures 1 and 2 in the PS67 Report.

3.2.3 Results from participating laboratories

In each of the PS64, PS65, PS66 and PS67 reports data provided by the participants are displayed in a series of tables and figures for comparison with each other and with the Benchmark Data. The Participant section provides five tables of data, the first outlining an overview of summary data including equipment and methodology used, the use of any chemical dispersants or pre-treatments, the percentage gravel, sand and silt/clay recorded as well as the participants' post-analysis sediment descriptions. The second table provides the raw sieve weights for each half-phi interval submitted by each participant including the less than 1mm weights for the sieve shaker base pan fraction and the wet-separated and oven dried fraction; in the third table the final laser data submitted by each participant is shown. The fourth and fifth tables show the results of the triplicate laser analysis supplied and the Coefficient of Variance of the D_{10}, D_{50} and D_{90}. These tables are accompanied by a series of graphs and bar charts which allow the results to be visually compared. Appendix 1 shows the data used to create the percentage gravel, sand, silt and clay bar-charts displayed in Figure 4 (PS64 and PS65) and Figure 7 (PS66 and PS67). The final merged data submitted by each participant and the benchmark laboratory are provided in Appendix2; the laser metadata for the Benchmark analysis are provided in Appendix 3.

3.2.3.1 Sixty-fourth distribution – PS64

There was generally good agreement for PS64 between the results for the replicates and those supplied by most of the participating laboratories, (see Figure 1). The result for

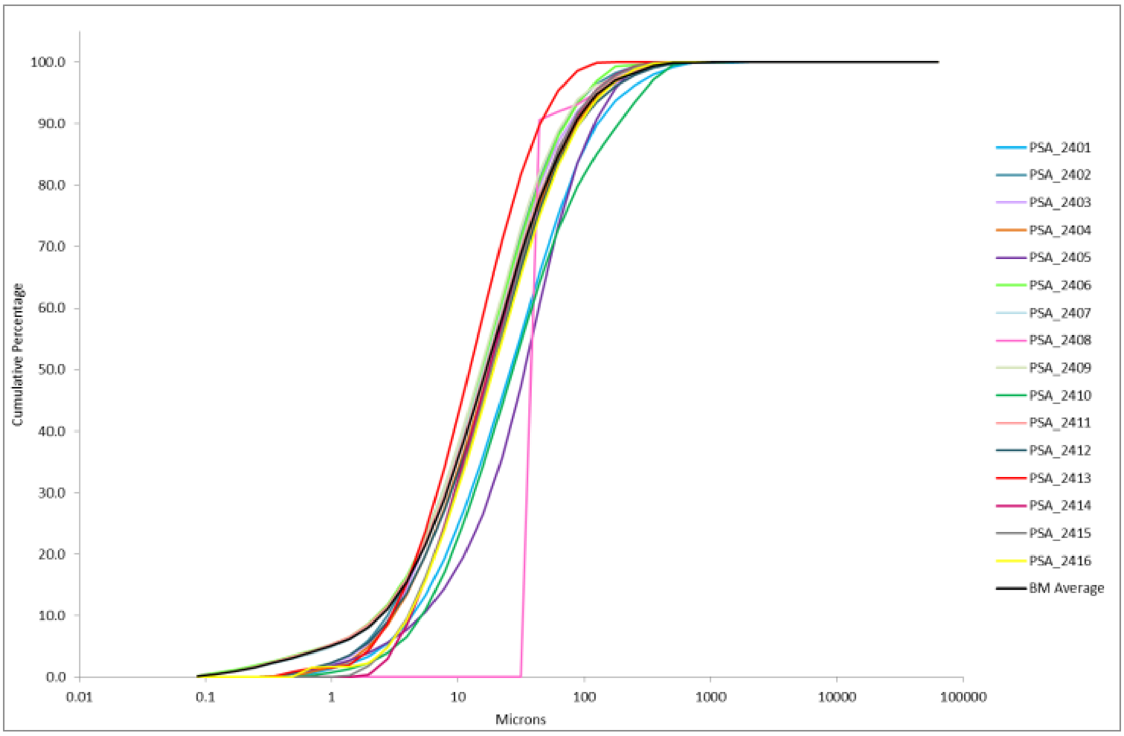

Figure 1. Particle size distribution curves for sediment distributed as PS64 (Figure 3 in PS64).

PSA_2408 follows a different distribution to other participants as they do not have access to a laser analyser and therefore are following a different methodology as stated in Table 5 in the PS64 Report.

Table 5 also shows the variation in data received from the participating laboratories; of the labs using a laser analyser the percentage of sand ranged from 10.3% (PSA_2413) to 39.0% (PSA_2405) and percentage mud ranged from 61.0% (PSA_2405) to 89.8% (PSA_2413). No participants used pre-treatments or chemical dispersants. Six participants (PSA_2401, PSA_2403, PSA_2406, PSA_2407, PSA_2411 and PSA_2412) chose to undertake sieve and laser analysis on this sample, the remainder only undertook laser analysis. Those that undertook sieve analysis found small amounts (0.04g – 0.08g) of sediment greater than 1mm, equating to a gravel percentage of 0.01% to 0.09% of the total sample, and recorded the sample as Slightly Gravelly Sandy Mud. The participants who only undertook laser analysis recorded the samples as Sandy Mud or a derivative such as Very Fine Sandy Very Coarse Silt or Coarse Silt.

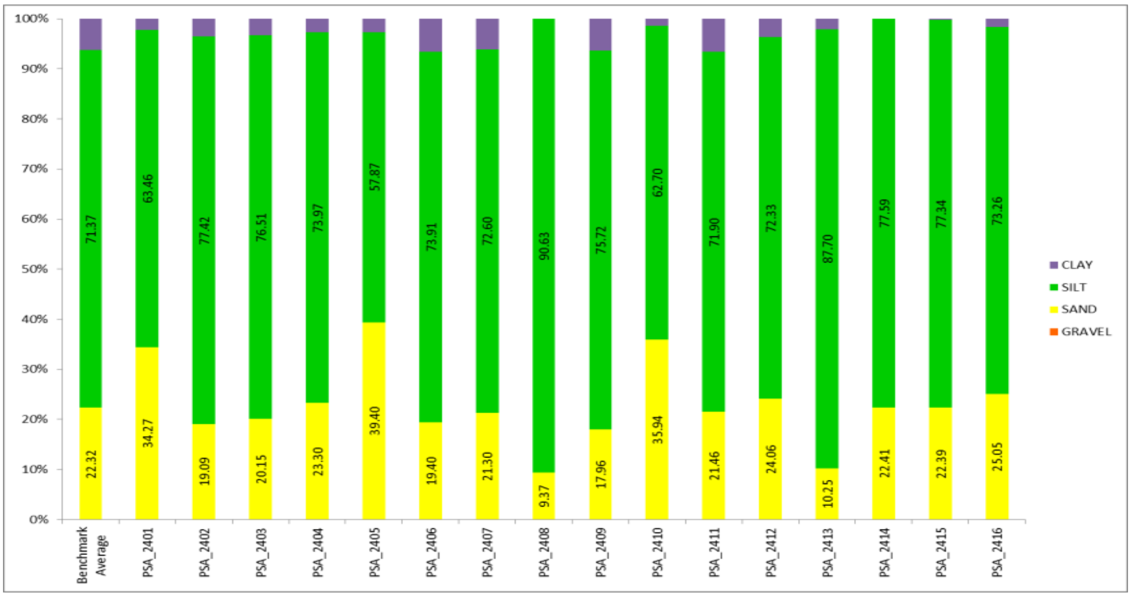

Figure 2. Bar charts showing the percentage gravel, sand, silt and clay for sediment distributed as PS64 (Figure 4 in PS64).

The sample showed a distinct variation in the amount of clay recorded in relation to the model of laser analyser used. Those participants using Beckman Coulter instruments recorded a higher percentage of clay than those using Malvern Mastersizer instruments, as shown in Figure 2. Participants PSA_2406, PSA_2407, PSA_2409 and PSA_2411 as well as the Benchmark Lab use the Beckman Coulter LS13 320 which uses a PIDS (Polarization Intensity Diffraction Scattering) system at the finer end, rather than diffraction, so provides better sensitivity than the Malvern system which employs diffraction of two different wavelengths of light (red and blue).

Of the participants following the NMBAQC methodology, three participants (PSA_2401, PSA_2405 and PSA_2410) recorded percentages of sand that were at least 5% higher than the Benchmark Average and one (PSA_2413) recorded percentage of sand that were at least 5% lower than the Benchmark Average. As a result these participants recorded at least ±5% difference in mud compared to the Benchmark Lab. Of the participants following the NMBAQC methodology participants PSA_2414 and PSA_2415 were the only two to record virtually no clay fraction. These differences are considered too large to be due to different laser instrument type alone and are possibly due to how the sample was prepared and/or presented to the laser analyser.

3.2.3.2 Sixty-fifth distribution – PS65

There was generally good agreement for PS65 between the results from the analysis of the benchmark replicates and those from the participating laboratories (see Figure 3). The distinct outlier (PSA_2415) does not process sediment greater than 1mm; therefore there is

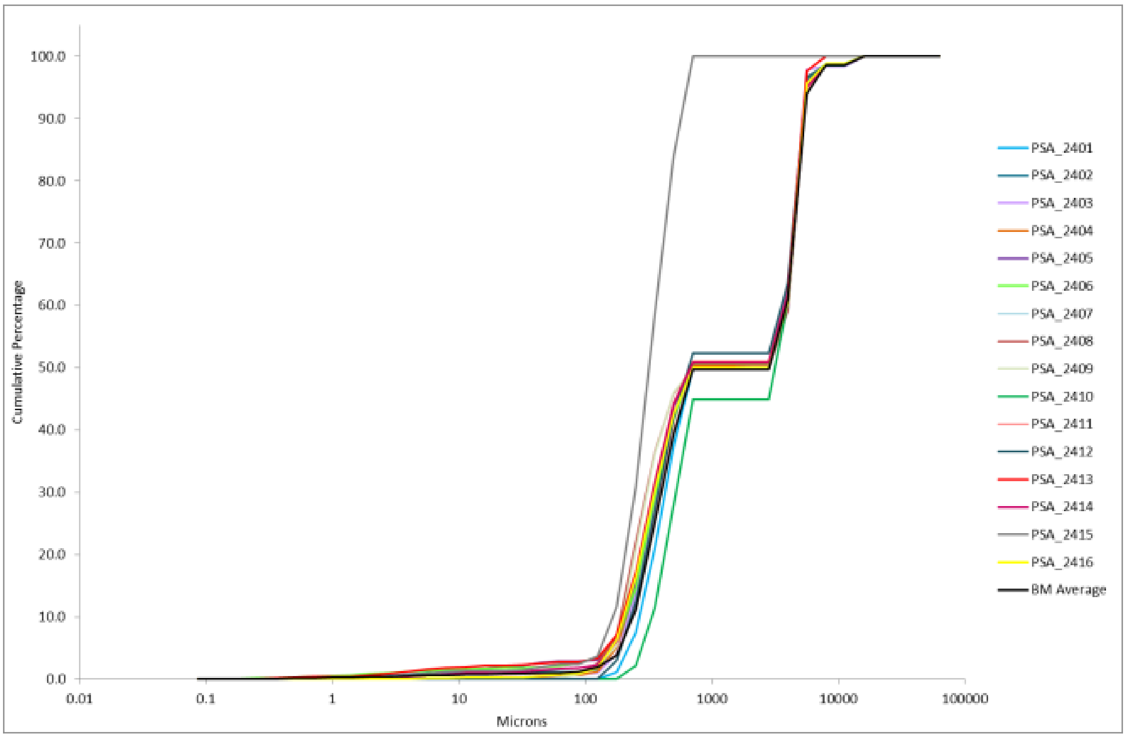

Figure 3. Particle size distribution curves for sediment distributed as PS65 (Figure 3 in PS65).

no sieve analysis for their sample. Participants PSA_2408 and PSA_2409 did not follow the NMBAQC methodology as they split the sample at 63microns rather than splitting at 1mm and undertaking laser analysis. The percentage of sediment less than and greater than 1mm recorded by the benchmark data and the majority of participants was very similar with approximately 50% of sediment less than 1mm and 50% greater than 1mm. The one anomaly was PSA_2410 who recorded 44.92% of sediment less than 1mm and 55.08% greater than 1mm. PSA_2410 also did not record any sediment smaller than 176.8microns, this explains why their cumulative percentage curve in Figure 3 is displaced from the others. The majority of participants recorded the sample as Sandy Gravel or a derivative e.g. Sandy Fine Gravel (PSA_2403) or Very Fine Gravel (PSA_2416).

The percentage mud recorded by participants was small (0.00% - 3.0%) and inconsistent; unlike PS64, laser instrument type appeared to have little impact on the percentage clay recorded. As the mud content was small it had little affect on the overall distribution of the sample.

3.2.3.3 Sixty-sixth distribution – PS66

There was a large amount of variation for PS66 between the results reported by the participating laboratories and those obtained for the benchmark replicates, as seen in Figure 4. Participant PSA_2415 did not analyse any sediment above 1mm and PSA_2408 did not

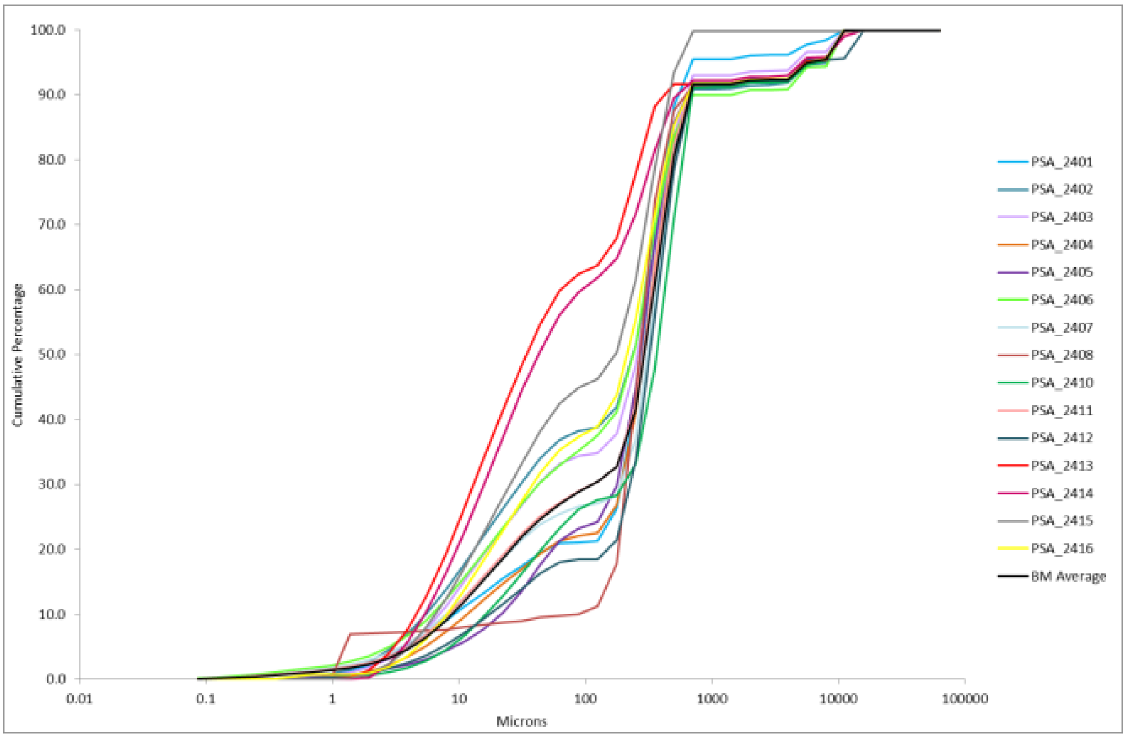

Figure 4. Particle size distribution curves for sediment distributed as PS66 (Figure 6 in PS66).

follow the NMBAQC methodology as they do not have a laser analyser. The overall percentage of Gravel was fairly consistent between participants (average = 8.07%, excluding lab PSA_2415), see Figure 5. Participant PSA_2401 recorded the lowest percentage gravel (4.54%); the raw sieve data provided in Table 5 of the PS66 Report show they may have only analysed a sub-sample of the replicate as the total weight of sediment above 1mm is recorded as 32.63g whereas the majority of participants recorded over 60g. However, their weight of less than 1mm material is similar to other participants thus causing the overall percentage gravel content to be lower. Percentage sieve data in Figure 8b (or Figure 4 of the PS66 Report) show that PSA_2412 appeared to record a higher amount of sediment on the 16 mm sieve (-4.5 to -4.0 size interval); however this was found to be a data entry error and the data had been displaced by a half-phi interval. Participants PSA_2411 and PSA_2414 also recorded sediment on the 16 mm sieve (-4.5 to -4.0 interval); however, as mentioned in sub-section *3.2.2* there was variation in the Benchmark sieve data for PS66 with Replicate 5 also recording 4.92g in this size interval, so therefore this was not considered to be an analytical error.

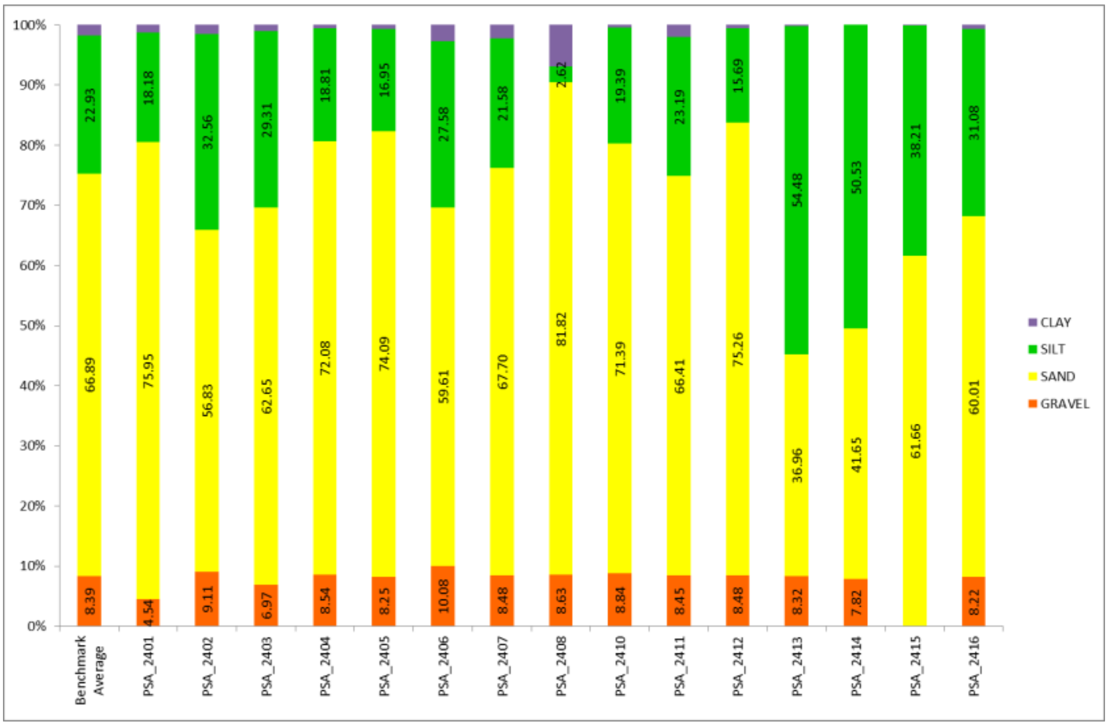

Figure 5. Bar charts showing the percentage gravel, sand, silt and clay for sediment distributed as PS66 (Figure 7 in PS66).

Although the majority of participants classified the sample as Gravelly Muddy Sand, there were differences in the proportions of mud and sand reported (see Figure 5). Participants

PSA_2413 and PSA_2414 classified the sample as Gravelly Mud, as can be seen in Figure 5, they both recorded a lower percentage of sand and higher silt content compared to other

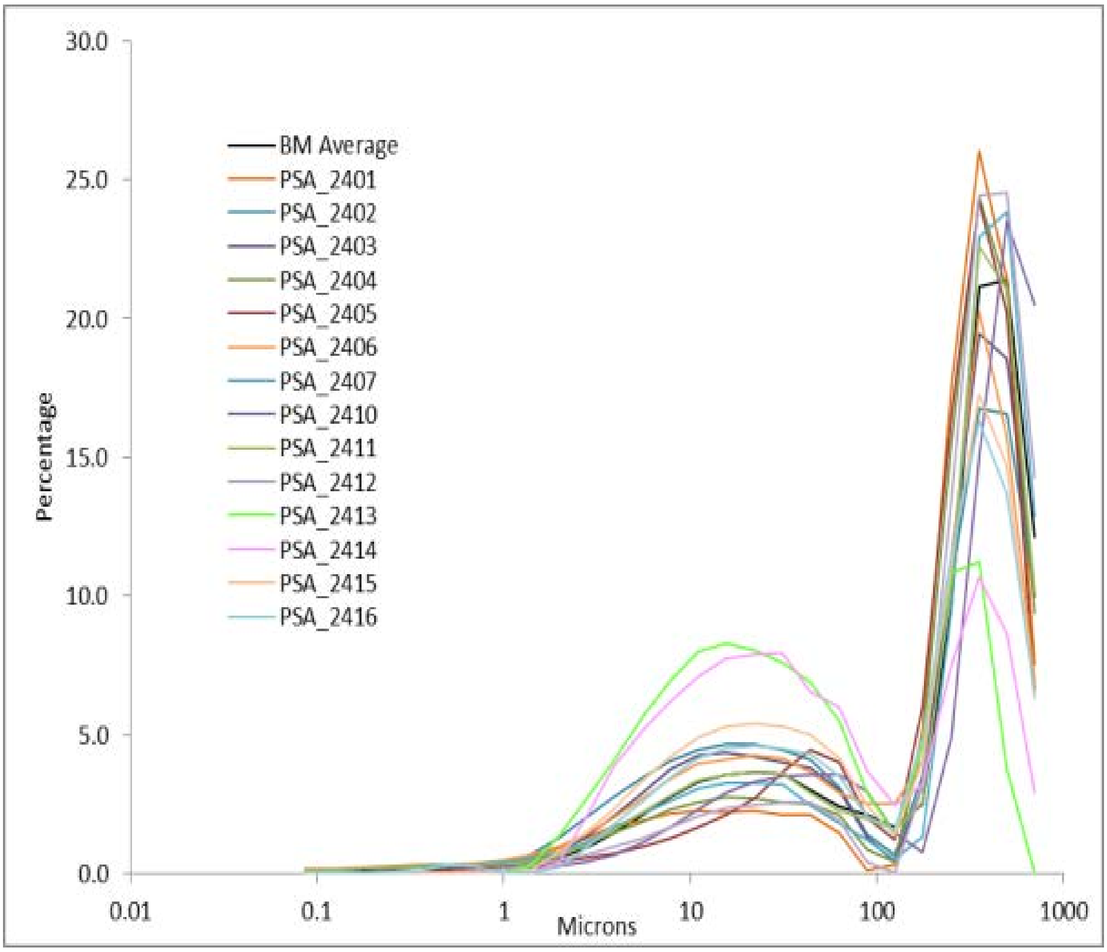

Figure 6. Differential Final laser data provided by each participant for sediment distributed as PS66 (Figure 5b in PS66).

participants and the benchmark data, both also recorded almost no clay content. The individual participant reports showing details of the Coefficient of Variation (CV) for the triplicate laser analysis undertaken by the participant showed that a lot of participant laser data showed poor reproducibility. Only three participants (PSA_2401, PSA_2407 and PSA_2411) provided CV's within the levels of 3% for the D_{50} and 5% for the D_{10} and D_{90}.

Percentage clay showed variation with laser instrument type, with the Beckman Coulter users (PSA_2406, PSA_2407, PSA_2411 and the Benchmark Lab) recording a higher percentage clay (average 2.18%) than those using the Malvern Mastersizer (average 1.40%).

3.2.3.4 Sixty-seventh distribution – PS67

There was very good agreement in results between the laboratories and the benchmark data (see Figure 7). All participants classified the sample as Gravel, with an average of 84.79% Gravel and 15.19% Sand. Participant PSA_2412 stated in Table 4 of the PS67 report that they recorded 0.27% mud, however, their final merged results (reproduced in Appendix 2 of the PS67 Report) do not record any mud. The sample was supplied as a dry sample; this may have caused some confusion as it would not be possible to undertake a wet separation at 1mm as stated by the NMBAQC methodology. As a result of this the sample only required dry sieve analysis. Five participants (PSA_2407, PSA_2408, PSA_2409, PSA_2410 and PSA_2411) chose not to follow the NMBAQC methodology and dry sieved down to 63microns. For those participants following the NMBAQC methodology and dry sieving to 1mm the process produced some less than 1mm material that was collected in the base pan. Participants PSA_2403, PSA_2404, PSA_2406 and PSA_2412 incorporated this base pan weight into their final data in the 0.0 to 0.5 phi size interval. Those that did not incorporate the less than 1mm base pan weight into the final data (PSA_2401, PSA_2402, PSA_2405, PSA_2413 and PSA_2416) ended up with the total sample weight in the Sieve section (Table 5) not matching the total sample weight in the Final data (Appendix 2). One participant (PSA_2414) chose to laser the less than 1mm base pan fraction thus recording 0.02% Mud.

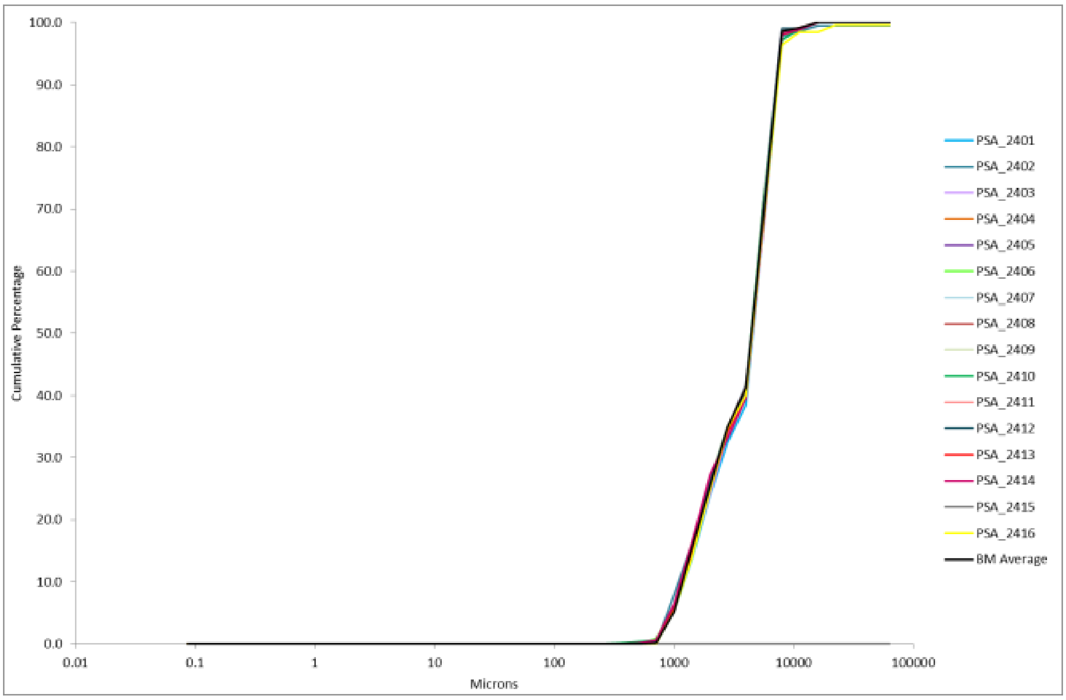

Figure 7. Particle size distribution curves for sediment distributed as PS67 (Figure 7 in PS67).

3.2.4 Discussion

The exercise reports show that the majority of participants follow the NMBAQC methodology for these exercises, but some do not. Participant PSA_2408 used different methodologies as they do not have access to a laser diffraction instrument. For PS67 a number of participants used the method of dry sieving to 63microns; although this is not strictly following the NMBAQC methodology it is a legitimate method for a dry sample containing 85% gravel as it is not possible to produce a sub-sample for laser analysis from the bulk sample. Participant PSA_2415 does not undertake analysis of sediment greater than 1mm so chose to only participate in the laser analysis.

Figure 8. Bar charts showing raw sieve data as percentage in each half-phi interval for (a) PS65, (b) PS66 and (c) PS67.

The three exercises that contained larger quantities of sediment greater than 1mm (PS65, PS66 and PS67) show that the dry sieve analysis (>1mm) undertaken by participants was generally in agreement (see Figure 8) even for those using alternative methods.

The main causes for concern were found in the laser analysis. For some participants (PSA_2405, PSA_2415 and PSA_2416) the laser replicates provided did not always sum to exactly 100% occasionally causing the final data provided not to sum to 100% either. There were only very small differences and it was not clear what was causing this problem. A possible explanation could be rounding errors; most participants provide laser replicate data as the raw laser output to multiple decimal places whereas PSA_2405 and PSA_2416 only provided data to 2 decimal places and PSA_2415 provided data to 3 decimal places.

It was apparent in the exercises that required laser analysis and had a significant mud fraction (PS64 and PS66) that there were differences in results depending on which laser instrument was being used. The Beckman Coulter instruments have a greater measurement sensitivity and were the only instruments capable of detecting particles below 11 phi. The results obtained using the Beckman Coulter instruments also showed a much greater degree of similarity to each other than those using generated using the Malvern instruments. There were still slight differences detected between the participants using Beckman Coulter instruments, however, and these could be due to differences in the samples supplied to each lab, different sub-sampling, sample dispersion and/or sample presentation procedures being used.

Figure 9 illustrates the variation in participant laser results for samples PS64, PS65 and PS66.

Laser metadata are very important in helping to identify where possible mistakes are being made and whether it is an issue with the laser or a sample preparation problem. For this reason, in the last scheme year provision of metadata was made a compulsory requirement. The majority of participants supplied laser metadata in the current year.

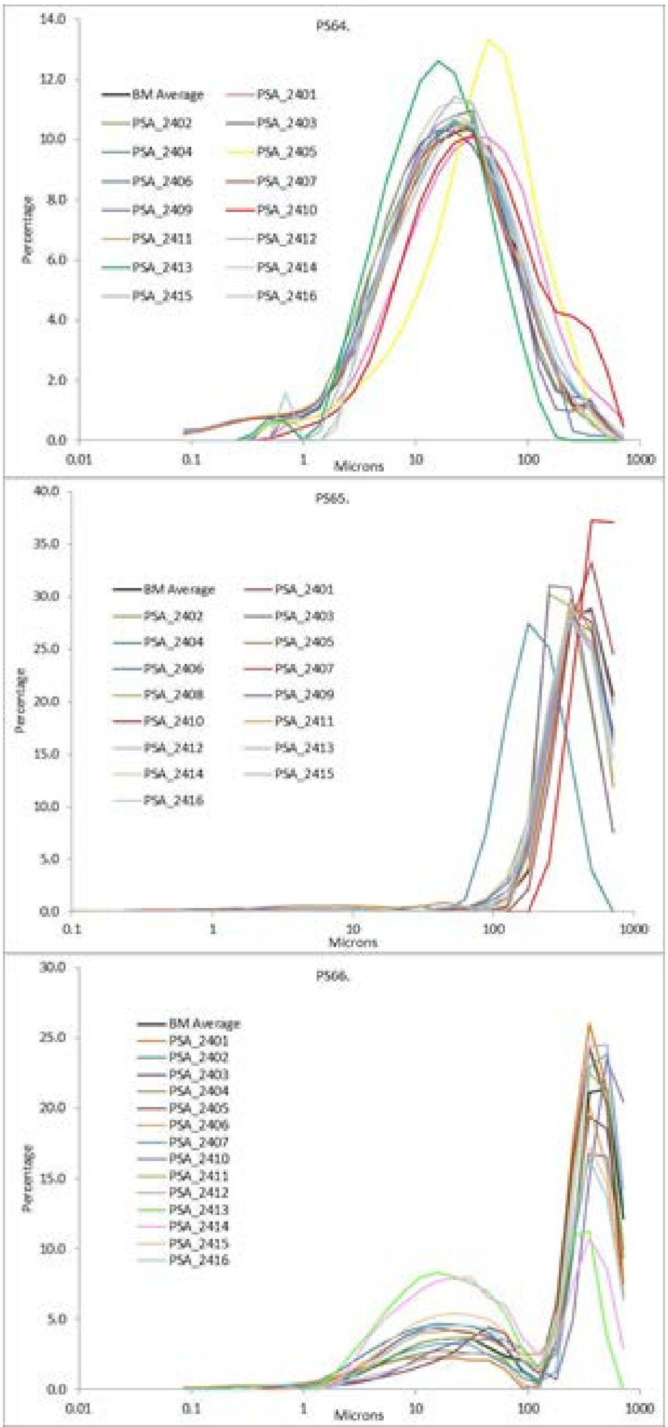

Figure 9. Differential final laser data provided by each participant for sediment distributed as PS64, PS65 and PS66.

Based on the information supplied, most participants used the Mie Theory model, as recommended in the NMBAQC Guidance, but two (PSA_2401 and PSA_2410) used the Fraunhoffer model and one (PSA_2403) used the General Purpose model. Of those labs using Mie Theory, the value for the 'imaginary' part of the refractive index (effectively an absorption index) was 0.1 for all participants expect one (PSA_2416), who use 0.01; the value for the 'real' component of the particle refractive index used by most participants was 1.55, although three participants (PSA_2403, PSA_2404 and PSA_2405) used 1.52, PSA_2414 used 1.59 and PSA_2416 used 1.45. The majority of participants using Malvern instruments had both the red and blue lights enabled, PSA-2410 consistently only had the red light enabled and PSA_2412 switched from having only the red light enabled for exercises PS64 and PS65, to having both the red and blue light enabled for PS66. These factors are probably mostly responsible for the high degree of variation in the laser size distributions seen in Figure 9. It is not always obvious why a result appears to be different without detailed laser metadata; for example, for PS66 one of the most deviant results provided was from PSA_2413, they only provided very basic metadata, including just the obscuration and fines extension used which makes it difficult to determine why their result deviates from the others. In addition to laser instrument set-up conditions and performance there are other factors that could be affecting the results, including sample preparation, sample dispersion methods and sample presentation to the laser instrument, about which no information has been provided.

3.2.5 Application of NMBAQC Scheme Standards and Laboratory Performance

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) and Water Framework Directive (WFD) monitoring programmes. With this aim, performance target standards were defined for certain Scheme modules and applied in 1996/97 (Scheme year three). 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. An overall summary of the data reported by each participant is presented in each of the PS exercise reports, and along with this each participant received a results table outlining their individual performance. In previous years 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.

As the Pass/Fail criteria are still under review for the PS exercises, in 2017/18 (Scheme year 24) a “Good” or “Review” flag has been issued for methodology and summary data, laser and sieve processing and data merging. This aims to highlight any potential errors but will not be used to assess the performance of a laboratory. Each laboratory was issued with a Statement of Performance certificate outlining their results and participation in the Scheme.

4. Particle Size Own Sample Analysis (PS-OS) module

4.1 Description

The Particle Size Own Sample (PS-OS) module is a relatively new module introduced in Scheme year 21 (2014/15) and is a training/ audit module. Participants’ “own” samples are re-analysed by the NMBAQC Scheme PSA contractor and the results are compared. The purpose of this exercise was to examine the accuracy of particle size analysis for participants’ in-house samples. In its first year (2014/15) the PS-OS exercises carried a trial Pass/Fail criteria based on the correlation between the participant data and the AQC data. After discussions between KPAL, APEM and the Scheme’s PSA Contract Manager (Claire Mason, Cefas), it was decided that a more simplistic approach to analysing the results would be more appropriate in identifying errors in participants’ results. The results were split into sieve processing, laser processing, data merging and whether a representative sample was supplied. Participants received a “Good” or “Review” flag based on their results. Where a “Review” flag was issued comments were supplied detailing problems that had arisen and where to find information to help address them.

4.1.1 Analysis required

Laboratories were requested to submit details of a survey with at least 12 samples from their previous year's Clean Seas Environment Monitoring Programme (formerly NMMP) samples, or similar alternative sampling programmes (if not responsible for CSEMP samples), along with the associated PSA data. Once these data were provided, three samples were randomly chosen by APEM Ltd to be re-analysed by the NMBAQC Scheme’s PSA contractor.

Spread-sheet based workbooks were distributed to each participating laboratory via email for each PS-OS exercise. These were to be returned to APEM Ltd via the NMBAQC Scheme email address (nmbaqc@apemltd.co.uk). 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.

In each workbook a written description of the sediment classification was to be recorded, a visual estimate was made prior to analysis and a post analysis classification based on the percentages of gravel, sand and silt/clay and the Folk (1954) terminology. Any use of hydrogen peroxide treatment or chemical dispersant was also to be recorded. Also requested was a breakdown of the particle size distribution of the sediment, expressed as a weight or weight percentage of sediment in half-phi (ϕ) intervals, as well as sieve and laser metadata to provide insight into laboratory procedures, especially for the laser analysis.

The different components of each PS-OS sample (< 1mm, > 1mm and laser sub-sample) were to be sent to APEM's Letchworth laboratory to be passed on to the NMBAQC Scheme PSA contractors. The two sets of results were then compared by APEM Ltd.

4.2 Results

4.2.1 General comments

Thirteen laboratories subscribed to the PS-OS module in 2017/18. Two of the thirteen lab codes belonged to the same participant to facilitate multiple PS-OS submissions due to the sub contraction of samples. All participants that subscribed to the module provided data and submitted samples for re-analysis.

Each laboratory received detailed comparisons of their data with the re-analysis results obtained by the NMBAQC Scheme's contractor. Where the original analysis was performed by the Scheme's contractor an external auditor was used to re-analyse the samples. Results were split into sieve processing, laser processing, data merging, whether a representative sample was supplied and whether the NMBAQC's methodology was being followed. At the end of each report participants received a "Good" or "Review" flag based on their results; where "Review" flags were issued, comments were made on errors that had arisen and links were provided to information to help resolve problems.

Laboratories generally provided workbooks with all the correct information. All participants except one (PSA_2405) provided all necessary fractions of their sample for re-analysis; participant PSA_2405 did not provide any laser sub-sample, therefore the dried < 1mm fractions were used for laser analysis but this required soaking for 48 hours to soften, before thoroughly mixing and subsampling for laser analysis.

There was generally good agreement between the participants and the AQC results, particularly in terms of basic sediment textural classification (see Figure 10).

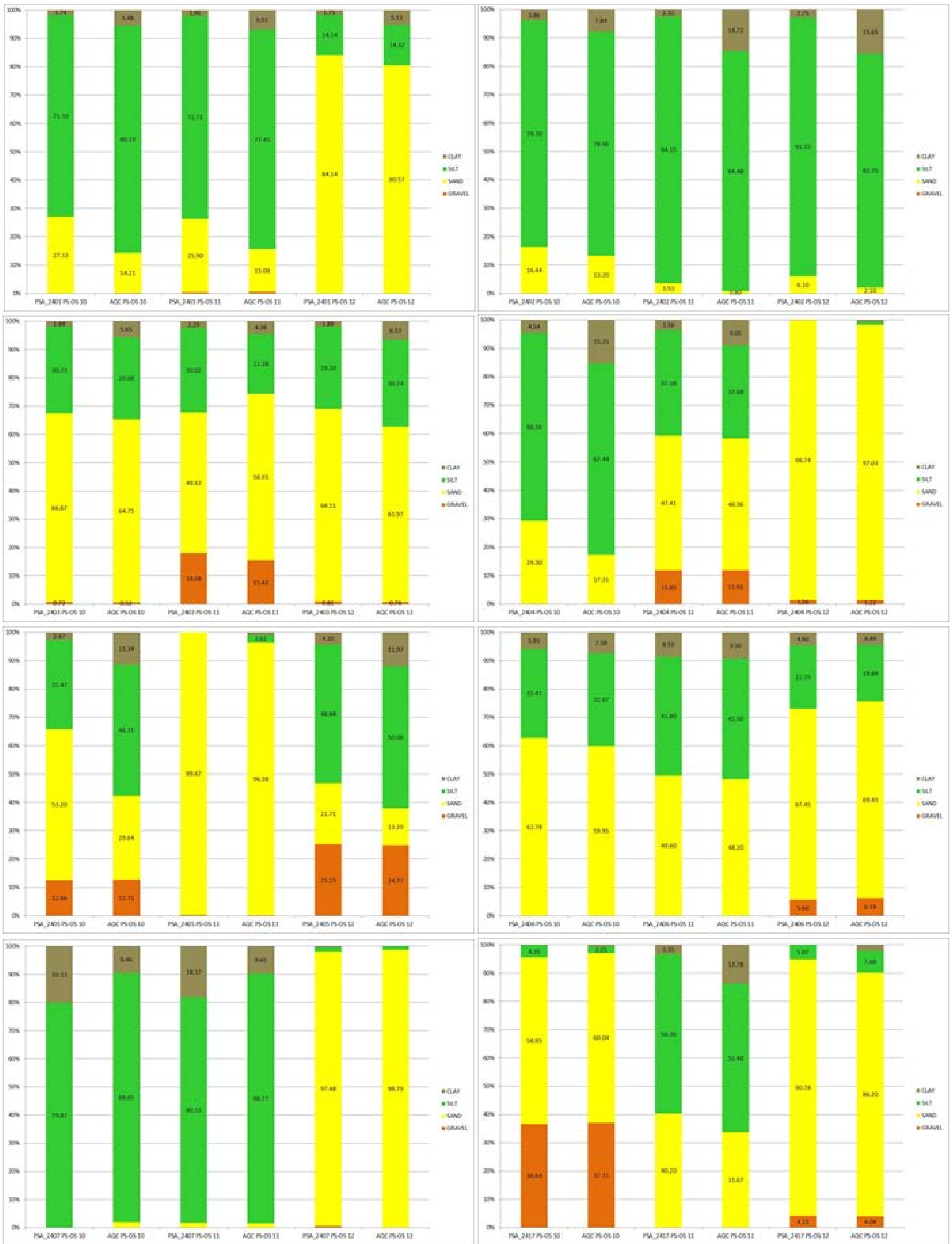

Figure 10a. Bar charts showing percentage gravel, sand, silt and clay for laboratories PSA_2401, PSA_2402, PSA_2403, PSA_2404, PSA_2405, PSA_2406, PSA_2407 and PSA2417participating in the PS-OS module.

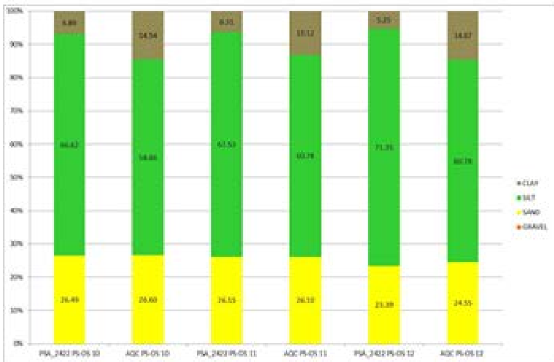

Figure 10b. Bar charts showing percentage gravel, sand, silt and clay for laboratories PSA_2418, PSA_2419, PSA_2420, PSA_2421 and PSA_2422 participating in the PS-OS module.

There were a few discrepancies in the sieve data but these are to be expected due to factors such as breakage of particles during repeat analysis and variations in sieving time and vibration amplitude. The AQC analysis of a few samples found small amounts of material greater than 1mm in samples where participants had undertaken laser analysis only, therefore sieve and laser analysis should have originally been carried out, however these small amounts of greater than 1mm particles had minimal effect on the overall distribution of the sample and were usually deemed not to be materially significant. One of the main issues with the participant data supplied was that laser data did not sum to 100%; this had a knock-on effect on the final merged data not summing to 100%. In some of the results there was a fair amount of variability in the laser analysis between the primary data and the Benchmark re-analysis; some of this variability can be explained by differing laser instruments used by the AQC lab and participants. As discussed earlier in this report, the Malvern Mastersizer 2000 and 3000 instruments do not have the same resolution as the

Beckman Coulter LS13320, especially at the finer end; the Beckman Coulter uses a PIDS (Polarization Intensity Differential Scattering) system at the bottom end, rather than diffraction, so provides better sensitivity than the Malvern system which employs diffraction of two different wavelengths of light (red and blue). Often the Beckman Coulter system reports higher mud content than the Malvern machines and the distributions produced by the Malvern tend to be more smoothed, and less able to identify discrete size modes. The output size distribution from the Malvern instruments machines is very dependent on the diffraction pattern interpretation model used; this can be selected by the operator as "General Purpose, Unimodal, and Multimodal etc." and can give rise to uncertainty. There is no such specification requirement with the Coulter instruments.

4.3 Discussion

As in previous years, the PS-OS module raised issues over the interpretation of the methodology set out in the NMBAQC Best Practice Guidelines (Mason, 2016), in particular how the laser analysis is undertaken. These guidelines, originally written in 2011, were based on the widespread use at that time amongst participants of Malvern Instruments laser diffraction instruments that have 15 – 25 second standard run times and generally are restricted to the analysis of material < 1mm in size. The original methodology suggested that:

1. A homogenised sub-sample of approximately 100ml is taken from the bulk sample for laser analysis (Laser Pot).
2. A small representative sub-sample is taken from the Laser Pot and passed through a 1mm sieve using as little water as possible (Replicate 1).
3. Replicate 1 is then run through the laser at the desired obscuration, producing three run results.

Steps 2 and 3 are then repeated to create Replicates 2 and 3, giving a final result of 9 runs to create the final laser data, the average of these 9 runs. The completion of nine analyses, and subsequent merging of results is necessarily a time consuming process, especially if standard run times longer than 15 to 25 seconds are used (e.g. 60 seconds is standard with Beckman Coulter instruments (if the PIDS system is activated).

It has been demonstrated by KPAL that, for the vast majority of samples, there is little practical benefit in routinely carrying out analysis of three replicate sub-samples if samples are homogenised properly both before the laser sub-sample is taken from the bulk sample and when the test sample is taken from the laser sub-sample, and the sample is adequately dispersed prior to presentation to the instrument. In relatively rare instances where samples consist very largely of > 1mm size material and it is impractical to obtain a representative laser sub-sample from the bulk sample, more consistent laser results can be obtained by taking a laser sub-sample from the wet separated < 1mm fraction of the sediment, rather than from the bulk sample.

Where samples display, or are suspected of, unstable behaviour, such as time-dependent agglomeration, one or more repeat runs of the same test sample should be carried out, and additional replicate test samples analysed. Sometimes this may require repeat runs of more than three replicates to fully characterise agglomerative behaviour, and to establish the best dispersal procedures required to obtain repeatable results (e.g. ultrasonic treatment before as well as during the analysis run, and/ or use of chemical dispersants). If the laser sub-sample is visually heterogeneous, and/ or during the preparation of the test sample it is observed that small amounts of sand are present within a mainly muddy matrix, two or more test samples should be analysed. Additionally for QA purposes, it is good practice to carry out at least duplicate analysis on 1 in 10 samples. The guidance has now been updated to incorporate most of these findings and recommendations, with some further follow up expected at future NMBAQC PSA workshops. The most recent version of the guidance can be viewed in Mason (2016). The returns for the 2017/18 PS-OS module showed that some laboratories, particularly those using Coulter instruments, in routine case work only run one laser test sample, with, for QA demonstration purposes, replicates run every 10th, 20th or

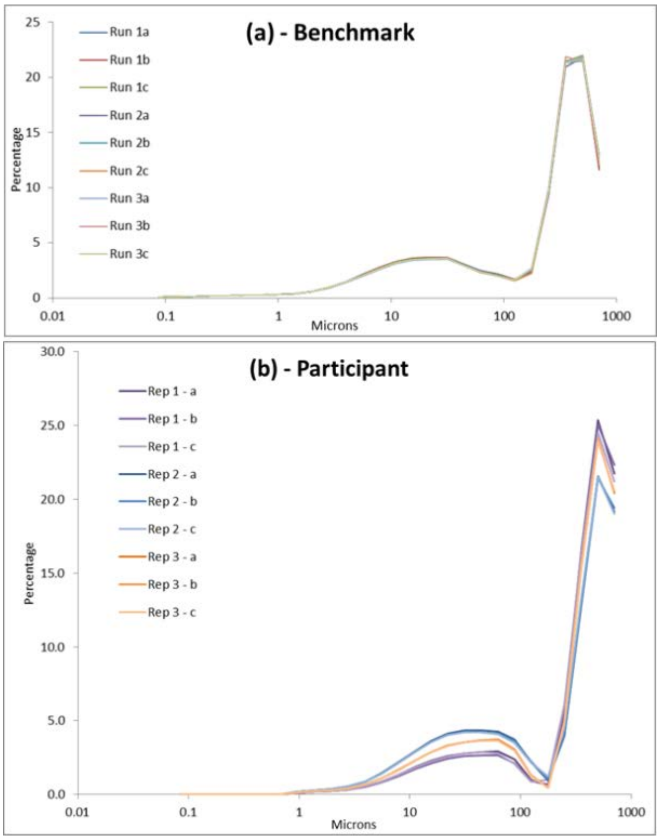

Figure 11. Differential laser data showing the difference in reproducibility between the Benchmark Data (Rep 3) and a participant for PS66.

50th sample, dependent on sediment type (less frequently for well sorted uniform sand samples than for poorly sorted muddy sand and muddy sandy gravel mixtures). The results obtained by KPAL, for the NMBAQC replicates samples prepared by APEM since 2014/15, demonstrate that the high degree of repeatability which can be obtained when strict analysis protocols are followed, and that a high degree of confidence can be placed in the results obtained for any individual analysis.

The PS-OS module also revealed that a few participants do not follow the NMBAQC methodology for routine samples. Participant PSA_2403 and PSA_2418 both stated that they were following alternative methods; PSA_2403 provided details of their in-house methodology whereas PSA_2418 did not. One participant (PSA_2420) used a different method as they do not have access to a laser analyser, in this case only the sieve and final data can be compared.

5. Conclusions and Recommendations

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

1. Laboratories should ensure that they follow the NMBAQC methodology when participating in the Particle Size (PS) Ring Test. The PS Ring Test is designed to test that all participants are getting comparable results when they follow the same methodology. It is therefore important that only the NMBAQC methodology (Mason, 2016) is used where possible and that results for 3 x 3 laser analyses are provided Participants who do not have access to a laser analyser will be permitted to use alternate methods for samples that contain sediment less than 1mm as long as the method used is detailed in the summary section of the workbook. Samples for the PS-OS module can be analysed following alternative in-house methods however these must be thoroughly described and the participant should be aware that re-analysis will be undertaken following the NMBAQC methodology. Samples provided for PS-OS which have been routinely analysed do not necessarily have to provide 3 x 3 laser analysis data but should show that appropriate QC checks have been carried out, including on the final data set. Participants will be reminded of this in the PS protocol document in the next Scheme year.

2. Participants should review their data prior to submission. Errors in datasets can often be spotted in the summary statistics, e.g. percentage gravel, sand and silt/clay,

before the data are submitted. All parts of the workbook should be double checked before submission to ensure that they are all filled in correctly. This will help eradicate typing and transcription errors.

3. The current NMBAQC Scheme Pass/Fail criteria for the PS modules are under review. Currently results are broken down for review, including methodology, sieve processing, laser processing, data merging and summary statistics. Laboratories then received a "Good" or "Review" flag based on their results; "Review" flags came with accompanying comments as to where mistakes have been made and how to correct them. This approach was thought to be more informative and would help participants to identify errors and correct any issues for future exercises. Research into more robust "Pass/Fail" criteria will continue, in the meantime the format will remain the same.

4. The PS and PS-OS module results both highlighted differences between the sensitivity of laser instruments. Comparison of laser data in the PS-OS and PS results showed that the Beckman-Coulter LS13320 instrument used by the AQC lab, which includes a Polarization Intensity Differential Scattering (PIDS) and gives enhanced measurement capability in the clay-size range (< 2 um) compared to other lasers models used by many of the NMBAQC scheme participants. The NMBAQC PSA workshop in December 2017 looked at possible ways to minimise the differences created by the use of different laser instruments and optical models, and the possibility of standardising so that all laboratories following the same procedures. It was agreed that the **recommended optical model is Mie Theory with values of 1.55 for the 'Real' and 0.1 for the 'Imaginary' components of the Particle Refractive Index, respectively** Experimental results have demonstrated that use of the Fraunhoffer optical model reduces the differences between laser instruments, albeit by loss of 'detail' within the very fine silt and clay size fractions. However, the potential suitability of using the Fraunhofer model to achieve greater inter-laboratory comparability will need to be explored in more detail when enough data have been collected. It has been suggested that in the next scheme year participants should submit data using both the Mie Theory and Fraunhoffer model to allow further assessment to be made. Obscuration will vary depending on sample type; only a small amount of mud is needed to reach an obscuration of 10%, and the presence of relatively small but potentially significant amounts sand may be missed; it may therefore be better to run at a higher obscuration where the presence of sand is observed during sample preparation. A gap can appear between the sieve and laser data in the final merged distribution if not enough sample is added to the laser to detect the sand. The 2017/18 workbook was modified to make the process of providing metadata simpler, and it is essential that participants complete the relevant sections. **The 2018/19 workbook will be modified to have the opportunity to provide laser data below 0.086um for those who wish to.**

5. A successful Particle Size Workshop was held at NLS in Leeds during December 2017 and an end-users workshop in Peterborough, June 2018. The December workshop included demonstrations by representatives of both major laser analyser manufacturers Malvern Instruments and Meritics on behalf of the Beckman Coulter, as well as presentations by the Benchmark Lab (KPAL – Prof. Ken Pye and Dr. Simon Blott) and scheme manager, Claire Mason (Cefas). The workshop demonstrated that there are still varying interpretations of the NMBAQC standard methodology and with changes in staff not all labs are fully aware or compliant with the procedures recommended in the Guidance. **In future scheme years it would be useful to consider either a practical workshop or making video to train new staff in the NMBAQC methodology** The June workshop focused on the end users of particle size data rather than those producing the data. The aim was to establish what the minimum requirements were both in terms of data quality and quality assurance for the laboratories producing data to meet the needs of the end users. As well as to produce quality data and metadata so that analyses can be reliably used for future studies.

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