NMBAQC

NE Atlantic Marine Biological Analytical Quality Control Scheme

Particle Size Analysis Component Annual Report
Scheme Operation 2016/2017 (Year 23)

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PARTICLE SIZE COMPONENT ANNUAL REPORT FROM APEM Ltd

SCHEME OPERATION – 2016/17 (Year 23)

NMBAQC

NE Atlantic Marine Biological Analytical Quality Control Scheme

Linked Documents (hyperlinked in this report):

Particle Size Exercise Results – PS60

Particle Size Exercise Results – PS61

Particle Size Exercise Results – PS62

Particle Size Exercise Results – PS63

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.
- 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 (PS) module followed the format of 2015/16. A series of exercises involved the distribution of test materials to participating laboratories and the centralised examination of returned data and samples.

The Particle Size Own Sample (PS-OS) module, introduced in the 2014/15 Scheme year, followed the same logistical format as the previous year. The changes made to the reporting format for 2015/16 (Scheme year 22) were maintained for Year 23. The report compared primary and AQC sieve and laser data separately along with data merging accuracy and assessed whether a representative sample was supplied for reprocessing. The purpose of this module was to examine the accuracy of particle size analysis for participants' in-house samples. The Particle Size Own Sample module is a training / audit module. Participants' samples are re-analysed by the NMBAQC Scheme PSA contractor and the results are compared. PS-OS exercises receive a "Good" or "Review" flag for each element; a "Review" flag is provided with additional comments highlighting errors and areas for improvement.

Fourteen laboratories signed up to participate in the 2016/17 PS module exercises (PS60, PS61, PS62 and PS63); five were government laboratories and nine were private consultancies. Thirteen laboratories signed up to participate in the PS-OS module exercises (PS-OS07, PS-OS08 and PS-OS09); nine were government laboratories and four 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

In previous years the Particle Size (PS) module 'Pass/ Fail' criteria were 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 annual report for 2009/10 (Scheme year 16) deemed the use of z-scores 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. Following this, the 'Pass/ Fail' criteria are currently under review and alternative flagging criteria are being trialled. For the 2014/15 year, evaluation of the PS module results included z-score calculations for each half-phi interval, multi-variate analysis in the form of dendrograms and MDS (multi-dimensional scaling) plots, particle size ternary diagrams to determine sediment distribution, as well as assessment of sieve and laser metadata. Following a review of the 2014/15 data, a new method of Pass /Fail was developed for 2015/16 (Year 22) using z-scores with robust statistics. Z-scores were calculated on statistics from the merged data, the statistics used were the D_{10}, D_{50}, D_{90} and Mean particle size in microns. Participants received a Satisfactory, Questionable or Unsatisfactory result based on the z-score. Results between -2.0 and 2.0 were Satisfactory, between ±2.0 and ± 3.0 were Questionable and results greater than ± 3.0 were Unsatisfactory. Participants then received a score and a Pass or Fail based on their results for each statistic. However, last year's results have shown that

even with robust statistics z-scores are not appropriate for creating "Pass" or "Fail" flags as variability in results can lead to participants receiving false "Pass" results. Mistakes in data merging were being concealed behind a final Pass or Fail result based on the final merged dataset. For 2016/17 (Scheme year 23) the reports will follow a similar format to that of PS-OS reports with each sample analysis section broken down for review, for example 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.

1.1.1 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', 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 2016/17 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.

2.1.1 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

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.

2.1.3 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 2016 each participant was given a confidential, randomly assigned 2016/17 (Scheme year twenty-three) 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 four in Scheme year twenty-three (2016/17) was recorded as PSA_2304.

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

2.2.1 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 (PS60), one coarser (PS63) and two diamictons (PS61 and PS62 were distributed in 2016/17. The samples were distributed in two stages; the first circulation (PS60 and PS61) was sent to participants on 15th May 2016 and the second circulation (PS62 and PS63) was sent on the 12th October 2016. For each circulation participants were given approximately 6 weeks to complete their analysis and send completed workbooks via email to APEM Ltd. PS60 and PS62 replicate samples were derived from natural marine sediments; PS63 replicates were artificially prepared from commercial aggregate materials; PS61 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.

2.2.1.1 Preparation of the Samples

The first PS circulation, PS60, was a mud collected from natural marine environments from 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 before it was cored into replicate samples

approximately 200 grams in weight. The second exercise, PS61, 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 sand from off the coast Eastbourne, 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 (PS62) was a diamicton sample made from natural sediments consisting of a mixture of gravel (>1mm) from Gravesend, pre-sieved (1.0mm) sand from Shoreham and pre-sieved (0.5mm) mud from the lower river Wandle, a tributary of the Thames. The gravel was collected during a survey and wet sieved over 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 (PS63) was created from known amounts of commercially acquired pea shingle split into half-phi intervals by dry sieving using a mechanical sieve shaker. For the mixed samples (PS61 and PS62) approximately 250g of water was added to help mix the sample together.

Five replicates were sent 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.

2.2.1.2 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 (Mason, 2011, (this version has since been updated, NMBAQC Best Practice Guidelines (Mason, 2016)), either in-house or using a subcontractor. A written description of the sediment characteristics was to be recorded, with a visual estimate pre-processing and using the Folk (1954) textural classification Triangles post-processing as well as the percentage gravel, sand and silt/clay and an indication of any peroxide treatment or chemical dispersant used. Also requested was a breakdown of the particle size distribution of the sediment, to be expressed as a weight or percentage of sediment at half-phi (ϕ) intervals.

The 2016/17 workbooks had the same format as the previous year; the second circulation (PS62 and PS63) had a slight modification in the sieve tab so that the 1mm weight was split into the oven dried less than 1mm and the less than 1mm from the base pan after dry sieving the sediment greater than 1mm. This was added to establish if participants were wet splitting the sample sufficiently; a high base pan weight would indicate poor wet separation of sediment greater than and less than 1mm. As in 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.

Approximately six weeks were allowed for the analysis of each pair of PS samples sent out (i.e. PS60 & PS61, PS62 & PS63).

2.2.2 Results

2.2.2.1 General comments

Fourteen laboratories subscribed to the exercises in 2016/17. For the first (PS60 and PS61) and second (PS62 and PS63) circulation all subscribing participants provided results.

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 (PS60, PS61, PS62 and PS63) have been reported to the participating laboratories; additional comments are provided below.

2.2.2.2 Analysis of sample replicates (benchmark data)

Five replicate samples of the sediment used for the four PS distributions were analysed by Kenneth Pye Associates Ltd (KPAL) to examine variability and establish benchmark data. 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 2016/17 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 Coefficient of Variation (CV) was calculated for the D_{10}, D_{50}, D_{90} and Mean 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 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.

Analysis of the replicates for Sample PS60 indicated an average composition of 21.13% sand and 78.87% mud, classified as "Sandy mud" according to the Blott & Pye (2012) scheme. Only laser analyses were required for this sample. The %CVs for the D_{90} and D_{50} were well within the limits, the D_{10} and D_{50} were slightly above the limits, this variability is more expected with natural sediments like PS60.The replicates were deemed to have good reproducibility, however this variability would be considered when assessing participant results. Results for the individual replicates are provided in Tables 1, 2, 3 and 4 and are displayed in Figures 1 and 2 (PS60 Report).

Sample PS61 was a mixed gravel and sand sediment and contained an average of 26.66% gravel, 72.13% sand and 1.21% mud, classified as a 'Gravelly sand' according to the Blott & Pye (2012) scheme. The replicates were analysed by dry sieving and laser analysis. The replicates showed extremely low variation, with %CV well below 3%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 (PS61 Report).

Sample PS62 was a diamicton and both sieve and laser analyses were required. The sample contained an average of 45.33% gravel, 48.87% sand and 5.80% mud and was classified as 'Muddy sandy gravel' according to the Blott & Pye (2012) scheme. The replicates showed extremely low variation, with %CV well below 3% 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 (PS62 Report).

Sample PS63 was a gravel sample and only required sieve analysis. The results showed an average of 100% gravel. The sediment is classified as 'Gravel' according to the Blott & Pye (2012) scheme. The replicates showed extremely low variation, with %CV well below 3% 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 (PS63 report).

2.2.2.3 Results from participating laboratories

In each of the PS60, PS61, PS62 and PS63 reports, Table 5 shows summary data i.e. the percentage gravel, sand and silt/clay recorded as well as the participants' post analysis sediment descriptions. The summary statistics were verified by APEM using the GRADISTAT program (Blott & Pye, 2001) based on the final half-phi frequency data provided by each laboratory, any errors would be highlighted in the individual participant performance review. Table 6 provides a summary of the > 1mm and < 1mm wet separation weights determined by each participating laboratory and the benchmark data. For PS60 and PS61 the < 1mm weight should have been the sum of the oven-dried < 1mm fraction plus the weight of sediment in the sieved > 1mm fraction base-pan. In PS62 and PS63 an extra line was added to differentiate between the oven dried <1mm sediment and the <1mm base pan sediment generated by dry sieving the >1mm. Table 7 shows a summary of the final laser data submitted by the participants in one phi intervals, and the total column indicates whether or not the laser data has been re-proportioned; correctly re-proportioned laser data should equal exactly 100%.

Figure 3 shows the particle size distribution curves for each of the exercises. Included in each of these figures, for comparison, are the mean distribution curves for the replicate samples obtained by KPAL. Figure 4 displays comparative bar charts of the major sediment components (% sand, gravel and mud) for each laboratory and for each exercise.

In PS60, Figure 5 shows a bar chart of the laser percentage retained in each phi interval and Figure 6 shows boxplots of the percentage sand and mud provided by each participant and the summary statistics (D_{10}, D_{50} and D_{90}) of the final merged data for each participant. For PS61, Figure 5 shows a bar chart of the sieve (>1mm) weights recorded by each participant and the average benchmark data, Figure 6 shows a bar chart of the laser percentage retained in each phi interval and Figure 7 shows the boxplots.

For PS62 and PS63, Figure 5 and 6 show the sieve (>1mm) data in the format of a bar chart (Figure 5) and a cumulative curve (Figure 6) and Figures 7 and 8 show the laser data in the format of a bar chart (Figure 7) and a cumulative curve (Figure 8). Figures 7 and 8 do not feature in PS63 as the sample consisted of gravel therefore only sieve analysis was required.

2.2.2.4 Sixtieth distribution – PS60

There was good agreement for PS60 between the results for the replicates and those supplied by the majority of the participating laboratories, (see Figure 3). Table 5 shows the variation in data received from the participating laboratories; percentages of sand ranged from 7.90% (PSA_2305) to 38.81% (PSA_2320) and percentage mud ranged from 61.19% (PSA_2320) to 92.10% (PSA_2305). One laboratory (PSA_2305) pre-treated their sample with the dispersant Sodium Hexametaphosphate. Participant PSA_2305 stated that they do not have a laser analyser therefore the sample was analysed using the Pipette method following the British Standard methodology. Participant PSA_2310 stated they were using an in-house methodology but did not provide any details on how this differed from the NMBAQC methodology. Other than PSA_2305, who do not have a laser analyser, all laboratories used laser analysis only. All participants provided summary data that was correct based on their final merged data. Table 7 shows that most participants provided re-proportioned laser data. PSA_2312 summed to 99.99% and PSA_2307 summed to 100.01% these are most probably rounding errors rather than data not being re-scaled.

Figure 3 showed that there were three participants whose cumulative distribution curves appeared to be different from the rest and the boxplots in Figure 6 showed that PSA_2305, PSA_2307 and PSA_2320 were outliers. As stated above, PSA_2305 were using a different methodology therefore it is not surprising that their results differ from the rest particularly as this was a fine, natural mud sample. PSA_2307 recorded a much lower percentage sand and higher percentage silt compared to the benchmark data and the majority of other participants. This could due to the sample not being thoroughly mixed before it was added to the laser; although the result is placed as an outlier it is still described as Sandy Mud. This participant requested another replicate sample to analyse and one of the benchmark replicates was sent for re-analysis. The re-analysis showed a slight increase in the percentage sand (13.05%), however this was still significantly lower than other participants; as no potential source of error could be found to explain this result without detailed information about the laser metadata it was decided that subsequent exercises for this lab would be closely monitored to check for any problems. PSA_2320 recorded a much higher percentage of sand and lower percentage of silt compared to the benchmark data and other participants this may be due in large part to dirty lenses and/ or low laser power, resulting in high background noise levels, without detailed laser metadata information it is unclear if this is definitely the reason for the poor result.

2.2.2.5 Sixty-first distribution – PS61

There was generally good agreement for PS61 between the results from the analysis of the benchmark replicates and those from the participating laboratories (see Figure 3). The percentage gravel recorded by the benchmark data and participants was very similar with only a difference of 2.48 grams between the highest (27.92g, PSA_2301) and lowest (25.44g, PSA_2306) values recorded. The main differences between participants were found in the laser analysis where the percentage of mud recorded varied from zero (PSA_2301 and PSA_2306) to 8.2% (PSA_2309). All participants recorded the sample as Gravelly Sand (post analysis) except for PSA-2309 who recorded it as Gravelly Muddy Sand. The percentage mud content of the four participants and benchmark laboratory using the Beckman Coulter laser analyser were much more consistent with each other (average mud=1.47%, standard deviation 0.51) compered to those using Malvern Mastersizer instruments (average mud=2.58%, standard deviation=3.06). A boxplot (Figure 7) revealed that participants PSA_2309 and PSA_2311 were outliers in the summary data (% sand and % mud) and participants PSA_2309 and PSA_2305 were outliers in the summary data (D_{10} and D_{50}). Participant PSA_2311 re-analysed some of their dried <1mm sediment after the interim results had been released and received results of 70.59% sand and 2.95% mud which was more in-line with the other participants and the benchmark data. However, there was a trade off in using the dried <1mm fraction for laser analysis that there was a slight reduction in the mode within the sand fraction. Participant PSA_2305 was an outlier for the D_{50} for the final merged data; this was not unexpected as they were following as different method due to not having a laser analyser. Participant PSA_2309 was an outlier for the percentage sand and mud as well as the D_{10} and D_{50}; this could possibly be due to not mixing the laser sub-sample thoroughly before adding to the laser or may be due in part to dirty lenses and/ or low laser power, resulting in high background noise levels, without detailed laser metadata information it is unclear what the reason is for this poor result. Two participants (PSA_2304 and PSA_2309) provided laser data as a percentage of the final merged data rather than the raw data. PSA_2312 provided laser data that had not been re-scaled to 100%; however the data had been re-scaled to calculate the final merged data.

2.2.2.6 Sixty-second distribution – PS62

There was generally good agreement for PS62 between the results from the analysis of replicates and those from the participating laboratories (see Figure 3), the main issues were found in the laser analysis. The percentage gravel recorded ranged from 40.24% (PSA_2309)

to 46.16% (PSA_2308), sand ranged from 36.08% (PSA_2308) to 53.14% (PSA_2312) and the silt/clay recorded ranged from 2.90% (PSA_2312) to 17.76% (PSA_ 2308). A verification of summary data with final merged data revealed that the summary data provided by PSA_2309 was incorrect, based on the final data provided the summary data should have been % gravel = 45.17, % sand = 44.05 and % mud = 14.79. Most participants recorded the sample as Muddy Sandy Gravel except for three (PSA_2304, PSA_2305 and PSA_2312) who recorded the sample as Sandy Gravel. The majority of participants followed the NMBAQC methodology and used both sieve and laser analysis to analyse the sample. One laboratory (PSA_2305) pre-treated their sample with the dispersant Sodium Hexametaphosphate. Participant PSA_2305 used the Pipette method following the British Standard Pipette methodology as they do not have access to a laser analyser. Participant PSA_2304 did not follow the NMBAQC methodology and sieved the sample to 63 microns. This explains why these two participants recorded a much lower percentage of mud (3.20%) compared to the majority of other participants and why they recorded the sample as Sandy Gravel as opposed to Muddy Sandy Gravel. Participant PSA_2312 also recorded a lower percentage of mud (2.90%) compered to other participants even though following the NMBAQC methodology, the low obscuration value of 6% used by this laboratory potentially leads to a non-representative result. PSA_2312 were sent a spare replicate to re-analyse at their request, however no results were re-submitted for this sample. Natural differences in the samples supplied to each participant could also be a factor; although we endeavour to make all the replicates identical, there will be variation when using natural materials to create the sample as with PS62. Two participants (PSA_2308 and PSA_2309) recorded a much higher percentage of mud compared to other participants, 17.76% and 15.70% respectively. PSA_2309 stated that they "… experienced technical difficulties with the Malvern Mastersizer during the laser granulometer analysis which meant that a portion of the sample aliquot was lost. With the limited volume of sample material remaining we completed the remaining replicate analysis however there was not enough to achieve optimum laser obscuration. (The Mastersizer terminated the SOP prematurely and discarded the sample before sample completion)"; this is a possible explanation for their poor result. Participant PSA_2309 did not provide re-scaled laser data (Table 7), the laser data was also not re-scaled when the laser and sieve data were merged as the final total weight of the merged data (840.29g) does not equal the total sample weight in the sieve data (848.10g).

2.2.2.7 Sixty-third distribution – PS63

There was good agreement in results between laboratories and between the laboratories and the benchmark data (see Figure 3). The majority of laboratories followed NMBAQC methods and used sieve analysis only. Participant PSA_2305 sieved down to 63 microns, PSA_2310 stated an "in-house" methodology was used but did not provide any details on how this differed from the NMBAQC method, however they attempted to perform laser analysis stating, "Although only a minor fraction of sediment fines was found during our analyses, this was analysed using the Mastersizer. However, due to the small amount available only one run (3 reads) was obtained". All participants recorded the sample as Gravel, with the majority stating 100% gravel. Participants (PSA_2302, PSA_03, PSA_2306 and PSA_2311) recorded the <1mm base pan weight in the 707micron category therefore recording small percentages of sand (on average 0.3%). Participant PSA_2301 split the base pan weight equally between the less than 1mm intervals, resulting in very small quantities of sand (0.003%) and mud (0.004%) being recorded. PSA_2304 had displaced the sieve data by 1 phi in the sieve tab of the workbook, this can be seen in Figures 5 and 6; this had however been corrected for the final merged data (Figures 3 and 4).

2.2.3 Discussion

The exercise reports show that the majority of participants follow the NMBAQC methodology for these exercises. Participant PSA_2305 used different methodologies as they do not have access to a laser, PSA_2304 followed an alternate method of sieving to 63 microns for exercise PS62 and PSA_2310 attempted laser analysis on exercise PS63 which consisted of gravel. All four exercises show that the sieve analysis (>1mm) undertaken by participants was generally in agreement even for those using alternative methods. The main causes for concern were found in the laser analysis. One participant (PSA_2309) did not re-scale laser data to 100% before merging with sieve data for exercises PS61 or PS62. It was apparent in all exercises that required laser analysis (PS60, PS61 and PS62) that there were differences in results depending on which laser instrument was being used. The Coulter instruments had a greater measurement of sensitivity and were the only instruments capable of detecting particles below 11 phi. The results of the Coulter instruments also showed a much greater degree of similarity to each other than those using the Malvern machines. There were still slight differences detected between the participants using Coulter instruments however 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.

Additional analysis undertaken on the laser replicates and metadata provided revealed there was a great deal of variation and some major problems. Using PS62 as an example, there was no consistency in whether red light alone or red and blue light were used by operators of the Malvern instruments and it was not clear which diffraction pattern interpretation model had been applied. Different laboratories apparently have used the multipurpose model, the uni-modal model, the bi-modal model and the poly-modal model, although in most cases this had not been specified. One participant has used the Fraunhofer optical model while others have apparently used the Mie model, but in the latter case most labs do not state the optical property values chosen. These factors are probably mostly responsible for the deviant laser distributions demonstrated by a number of participants. A few participants queried results and asked for additional replicates to re-analyse. It is not always obvious why a result appears to be different without detailed laser metadata, this is an issue that needs to be addressed before the next scheme year.

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) 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. 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 2016/17 (Scheme year 23) 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.

2.2.4.1 Laboratory Performance

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 based on methodology and summary data, laser processing, sieve

processing and data merging. A "Good" or "Review flag was issued based on comparison of data with other participants and the benchmark data. The "Pass/Fail" criteria are still under review and are not to be used to assess the performance of a laboratory. Each laboratory was issued with a Statement of Performance outlining their results and participation in the Scheme.

2.3 Particle Size Own Sample Analysis (**PS-OS**) module

2.3.1 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.

2.3.1.1 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 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.

2.3.2 Results

2.3.2.1 General comments

Fourteen laboratories subscribed to the PS-OS module in 2016/17. Two of the fourteen lab codes (PSA-2316 and PSA_2317) belonged to the same participant to facilitate multiple PS-OS submissions due to the sub contraction of samples. One potential participant (PSA_2318) did not submit any own samples for reanalysis, but sent an email confirmation of their non-participation. Three participants (PSA_2315, PSA_2316 and PSA_2317) opted to use their PS-OS subscription for bespoke AQC of a project's data outside of the official Scheme as their data would not be ready in time to be reported within the routine timescales of the PS-OS module.

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. Seven participants (PSA_2302, PSA_2303, PSA_2306, PSA_2309, PSA_2312, PSA_2313 and PSA_2319) provided all necessary fractions of their sample for re-analysis, however the samples for PSA_2303 were considered by the AQC laboratory to be too small to be

representative of sediment in the field. Participant PSA_2320 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. Participant PSA_2314 provided freeze dried bulk samples, but they did not supply any >1mm or <1mm fractions, even though gravel and whole shells were present in two of the samples. For the re-analysis the AQC lab wet-separated the bulk sample provided over a 1mm sieve and carried out the usual NMBAQC methodology. Participant PSA_2214 reported that they were only interested in the < 1mm fraction; therefore although there was > 1mm sediment present in the samples it had not been analysed. Participant PSA_2314 were also not following the NMBAQC methodology, samples were instead freeze dried and screened over a 2mm sieve before being presented to the laser analyser. Participant PSA_2311 also used an alternate method, (details can be found in 7.3.2.2 Discussion); comments from the AQC lab were that the laser subsamples had been supplied in large bags which appeared to have been the original sample bags. It is possible therefore that the majority of the sediment had been removed for wet separation and sieving, leaving a small amount in the bag for laser analysis which might not be representative of the original bulk sample. It does not appear a separate laser subsample was taken from the bulk sample, after thorough mixing, as required under NMBAQC guidelines.

There was generally good agreement between the participants and the AQC results, particularly in terms of basic sediment textural classification. 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 materially significant. The majority of participants merged data correctly with only one participant not re-proportioning laser data to 100%; this had a knock-on affect on the final merged data. In some of the results there was a fair amount of variability in the laser data; some of this variability can be explained by differing laser instruments used by the AQC lab and participants. The Malvern Mastersizer 2000 and 3000 instruments do not have the same resolution as the Coulter LS13320, especially at the finer end; the 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 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.

2.3.2.2 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 over 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), which are used by some NMBAQC Scheme participants).

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 2016/17 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 10^{th}, 20^{th} or 50^{th} 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. One participant (PSA_2319) 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. One participant (PSA_2314) freeze-dried samples and separated over a 2mm sieve before presenting to the laser. Malvern instruments have problems with coarser particles (> 1mm) getting stuck in the pipework; this is why the NMBAQC guidance specifies

that sediment should be wet split at 1mm and only particles <1mm presented to the laser analyser.

Participant PSA_2311 used a differing methodology; sediments from each sample were homogenised and divided into three portions. The first portion of approximately 10% of the sample was used for determination of particle sizes below 1mm. A sub-sample from this 10% was pre screened through a 1mm sieve before being presented to the laser analyser. The second portion (Part A) of approximately 45% of the sample was used to determine the moisture content of the sediment. The third portion (Part B) of approximately 45% of the sediment was used to determine the particle size distribution above 1mm. This was weighed and the weight was converted to dry weight using the results from the first (Part A) portion. Part B was then wet sieved over a 1mm sieve under running water (with the <1mm fraction discarded). The retained material was dried then separated using nested stainless-steel sieves. Each size fraction was weighed and the weights expressed as a percentage of the dry weight of the total sub-sample. This methodology means that the whole sample has not been analysed as only 45% of the sample is used to determine the amount of sediment >1mm, NMBAQC guidelines state that the whole sample should be processed not a sub-sample.

3. 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 their PS results are reported in the requested format. Data should be provided at half-phi intervals to enable the direct comparison of data from all participants and simplify the creation of cumulative curve figures. The workbook was modified for use in 2014/15 to assess whether laboratories are merging data correctly in their in-house methods. It is therefore even more important that that data are reported correctly. Raw sieve data should be reported in grams, with the > 1mm and < 1mm wet separated fraction weights provided. For Scheme Year 24 the <1mm weight will be split into oven dried weight and base pan weight to assess the wet splitting process. Raw laser data should be provided re-scaled to 100% and reported as volume percentages. Final merged data should ideally be reported in percentage of final weight.

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 it is 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. The 2016/17 (Scheme year 23) reports followed a similar format to that of the PS-OS reports with each section 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. Some participants voiced frustration over the change in result format stating it makes it difficult to carry out any trend monitoring on submissions as they are unable to compare them like for like. However, results from 2015/16 showed that even with robust statistics z-scores are not appropriate for creating "Pass" or "Fail" flags as variability in results can lead to participants receiving false "Pass" results**. Research into more robust "Pass/Fail" criteria will continue, in the meantime the format will remain the same for Scheme Year 24 (2017/18)**.

4. The 2016/17 PS and PS-OS module 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) which gives enhanced measurement capability in the size range 0.4 and 0.04 microns, indicates higher clay content compared to other lasers models used by many of the NMBAQC scheme participants. It is therefore even more important that participants provide metadata regarding the laser model and optical model used, and about the dispersion methods, whether or not ultrasonics were used before or after the run in addition to the possible use of chemical dispersant. Although laser models will not be directly linked to participants, in order to keep participant confidentiality, the range of laser models used will be specified in future reports. As well as this, the possibility of developing conversion factors between laser sizers will be explored when enough data have

been collected. **It is essential that participants supply detailed laser metadata and the 2017/18 workbook will be modified to make this process simpler.**

5. The 2016/17 PS-OS module highlighted that participants still do not always supply the samples in the requested format, i.e. dried > 1mm fraction, dried < 1mm fraction and a laser subsample taken from the bulk sample. The NMBAQC guidance has been updated with more detailed advice on how to store samples; these amendments are included in the guidance and can be viewed in Mason (2016). **At the start of Scheme Year 24 participants will be reminded that samples should be supplied as a dried >1mm fraction, dried <1mm fraction and a laser sub-sample.**

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