NMBAQC

The National Marine Biological Analytical Quality Control Scheme

Particle Size Analysis Component Annual Report
Scheme Operation 2014/2015 (Year 21)

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PARTICLE SIZE COMPONENT ANNUAL REPORT FROM APEM Ltd

SCHEME OPERATION – 2014/15 (Year 21)

Linked Documents (hyperlinked in this report):

Particle Size Exercise Results – PS52

Particle Size Exercise Results – PS53

Particle Size Exercise Results – PS54

Particle Size Exercise Results – PS55

1. Introduction

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

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

The 2014/15 NMBAQC scheme year saw the administrative contractor for the Particle Size component change from Thomson Unicomarine Ltd to APEM Ltd.

The Particle Size (PS) module followed the format of 2013/14. A series of exercises involved the distribution of test materials to participating laboratories and the centralised examination of returned data and samples.

As well as the regular PS module, the 2014/15 scheme year introduced a new module into the particle size component; the Particle Size Own Sample (PS-OS) module. The purpose of this exercise 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 will carry pass/fail criteria; these criteria will be reviewed and assessed in this annual report. In this Scheme year 21, (2014/15), results will not be used to assess the performance of a laboratory.

Fifteen laboratories participated in the 2014/15 PS module's exercises (PS52, PS53, PS54 and PS55); six were government laboratories; nine were private consultancies. Eight laboratories participated in the PS-OS module's exercises (PS-OS01, PS-OS02 and PS-OS03); six were government laboratories and two were private consultancies.

To reduce potential errors and simplify administration Lab Codes were assigned with a prefix to determine the Scheme component; all codes for 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 Summary of Performance

This report presents the findings of both the PS and PS-OS modules in the Particle Size Analysis component for the 2014/15 year of operation of the National Marine Biological Analytical Quality Control (NMBAQC) Scheme.

The analytical procedures of this module were the same as for the 2013/14 scheme year. The results for the four exercises are presented and discussed. Comments are provided on the performance for each of the participating laboratories in each of the exercises.

In previous years the Particle Size exercises (PS) '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.

Comments are provided on the individual performance of the participating laboratories in each of the above components.

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 Schemes modules and details the resulting flags where appropriate. These statements were first circulated with the 1998/1999 annual report, for the purpose of providing proof of Scheme participation and for ease of comparing year on year progress.

2. Summary of PSA Component

2.1 Introduction

The two 2014/15 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 September 2014 each participant was given a confidential, randomly assigned 2014/15

(Scheme year twenty-one) 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-one (2014/15) was recorded as PSA_2104.

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 (PS52), two coarser (PS53 and PS54) and one diamicton (PS55) were distributed in 2014/15. The samples were distributed in two stages; the first circulation (PS52 and PS53) was sent to participants on 15/09/2014 and the second circulation (PS54 and PS55) was sent on the 19/12/2014. For each circulation participants were given approximately 6 weeks to complete their analysis and send completed workbooks via email to APEM Ltd. PS52 replicate samples were derived from natural marine sediments; PS54 replicates were artificially prepared from commercial aggregate materials; PS53 and PS55 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, PS52, was muddy sand collected from natural marine environments around Swanage. Approximately 30 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 520grams in weight. The second exercise PS53 was a mixture of the pre-sieved (0.5mm) muddy sand from Swanage and known quantities commercial aggregate (pea shingle) dry sieved at half phi intervals. The third exercise sample (PS54) was artificially created from commercially acquired pea shingle that was split into half phi intervals by dry sieving in the sieve shaker. The final sediment (PS55) was diamicton sediment artificially created from combined natural sediments (sand from Swanage and mud from Barry Island) and commercially acquired materials; 200g 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 a laser was required, these *replicate*s were analysed using a Coulter LS230 laser size analyser. 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's best practice guidance for particle size analysis to support biological data (Mason, 2015), either in-house or using a subcontractor. A written description of the sediment characteristics was to be recorded (pre-processing and post-processing using the Folk Triangle) 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 in half-phi (ϕ) intervals.

The 2014/15 scheme year incorporated some changes in the PS workbook. The "Final Merged Data" tab no longer auto-filled; this was to establish whether or not laboratories were merging data correctly in their in-house methods. Two additional tabs were included, "Participant Sieve Metadata" and "Participant Laser Metadata", these provided insight into laboratory procedures, especially for the laser analysis. Data provided in theses tabs were for analytical purposes only and were not published in the interim results.

Approximately six weeks were allowed for the analysis of each pair of PS samples sent out (i.e. PS52 & PS53, PS54 & PS55).

2.2.2 Results

2.2.2.1 General comments

Fifteen laboratories subscribed to the exercises in 2014/15. One of the laboratories did not submit returns for any of the exercises and one pulled out due to conflicts of interest as they sub-contracted their PS analysis to the same laboratory that was analysing the benchmark replicates. Resulting in returns from thirteen laboratories.

Most participating laboratories now provide data in the requested format, although some variations remain. As previously reported, it should be remembered that the results presented may be from a more limited number of analytical laboratories than is immediately apparent since this component of the Scheme is often sub-contracted by participants to one of a limited number of specialist laboratories. One laboratory provided two sets of results

run by two different analysts for PS52 and PS53. Due to samples being frozen on receipt one lab was sent a second set of exercises PS54 and PS55 and provided two sets of results, one from the frozen sample and one from the non-frozen sample. Detailed results for each exercise (PS52, PS53, PS54 and PS55) 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 were analysed where required using Endecotts British Standard 300 mm and 200 mm test sieves, Endecotts EFL 2000/2 sieve shaker and a Beckman Coulter LS230 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 Year 21 was undertaken only using a laser diffraction instrument.

Analysis of the replicates for Sample PS52 indicated an average composition of 76.82% sand and 23.18% mud, classified as 'Muddy Sand' according to the Folk (1954) scheme and the Blott & Pye (2012) scheme. The data for individual replicates showed light variation in the size range between 3.0 and 7.0phi. This is to be expected with natural sediment like PS52. Results for the individual replicates are provided in Tables 1, 2 and 3 and are displayed in Figure 1 (PS52 Report).

Sample PS53 contained an average of 52.03% gravel, 47.16% sand and 0.81% mud, classified as a 'Sandy Gravel' according to both the Folk (1954) and Blott & Pye (2012) schemes. Both sieve and laser analyses were undertaken for this exercise. The replicates showed extremely low variation. Results for the individual replicates are provided in Tables 1, 2 and 3 and are displayed in Figure 1 (PS53 Report).

Sample PS54 comprised an artificial gravel sediment. The replicates were analysed by dry sieving only, no laser analysis was required. The replicates showed a very high degree of similarity, with an average of 100 % gravel. Results for the individual replicates are provided in Tables 1, 2 and 3 and are displayed in Figure 1 (PS54 Report).

Sample PS55 comprised an artificial mixture of gravel, sand and mud. Sieve and laser analysis were both required to analyse this sample. The results showed a very low degree of

variation with an average of 79.99 % gravel, 3.74% sand and 16.26% mud. The sediment is classified as 'Muddy Gravel' according to the Folk (1954) scheme and as 'Very Slighty Sandy, Slightly Muddy Gravel' according to the Blott & Pye (2012) scheme. Results for the individual replicates are provided in Tables 1, 2 and 3 and are displayed in Figure 1 (PS55 Report).

2.2.2.3 Results from participating laboratories

In each of the PS52, PS53, PS54 and PS55 reports, Table 1 provides a summary of the > 1mm and < 1 mm wet separation weights determined by each participating laboratory and the benchmark data. 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. Table 2, in the case of PS52, PS53 and PS55, provides the percentage of sediment (by volume) <1mm in whole phi categories, taken from the "final laser" tab in the exercise workbooks. These percentages are taken before merging with any sieve data has occurred. Table 3 in PS52, PS53 and PS55, and Table 2 in the case of PS54; show the summary merged statistics for each laboratory and the benchmark data. Where the summary statistics were not provided by participating laboratories they were calculated by APEM Ltd (highlighted in the tables in red text). 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. Table 4 (PS52, PS53 and PS55) and Table 3 (PS54) show a summary of the z-scores for each half-phi percentage frequency category; those greater or less than ±1.96 (95% confidence level) are highlighted in yellow.

Figure 2 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 3 in each exercise shows particle size ternary diagrams depicting which Blott and Pye (2012) textural group the samples analysed by each laboratory fell into. Figure 4 displays comparative bar charts of the major sediment components (% sand, gravel and mud) for each laboratory and for each exercise.

2.2.2.4 Fifty- second distribution – PS52

There was good agreement for PS52 between the results for the replicates and those supplied by some of the participating laboratories, although the latter showed considerable variation (see Figure 2). One laboratory (PSA_2109) pre-treated their sample with a chemical dispersant. Although they stated NMBAQC Scheme methods as their methodology, PSA_2109 did not follow the procedure correctly as the data were not provided in half-phi

intervals, resulting in plateaus in their cumulative distribution curve shown in Figure 2. Seven of the laboratories used sieve and laser analysis, four laboratories just used laser analysis and one laboratory only used sieve analysis. Table 3 shows the variation in data received from the participating laboratories; rounded percentages of sand ranged from 75.0% (PSA_2105) to 100.0% (PSA_2107), and percentage mud ranged from 0% (PSA_2107) to 25% (PSA_2105). PSA_2107 appeared to have submitted data for PS52 as PS53 and vice-versa with the sieve data mixed up between samples. They were contacted and re-submitted data at a later date; the recorded percentages for the re-run were: 81.4% sand and 18.6% mud. Participants PSA_2110 and PSA_2111 did not provide the summary data required for Table 3 so these were calculated by APEM based on the final merged data supplied. PSA_2112 had calculated the percentages of sand and silt/clay incorrectly by one per cent (PSA_2112, sand = 75.2%, mud = 24.8; APEM verification, sand = 74.2%, mud = 25.8%).

2.2.2.5 Fifty-third distribution – PS53

There was generally good agreement for PS53 between the results from the analysis of the benchmark *replicates* and those from the participating laboratories (see Figure 2), although three laboratories stand out from the rest. Participant PSA_2113 reported a higher percentage of silt/clay (5.7%), as seen in the bar chart in Figure 4. This participant PSA_2113 also appears to have displaced the data by a half-phi either side of 0 phi. Table 3 shows that PSA_2107 recorded a higher percentage of gravel (75.5%) and a lower percentage of sand (22.6%) than the majority of laboratories. However, as mentioned in section 2.2.2.4, there had been some mix ups between PS52 and PS53. The re-run PS53 sample recorded 54.1% gravel and 45.9% sand, which was in-keeping with the other laboratories. Participants PSA_2110 and PSA_2111 did not calculate the percentage gravel, sand and silt/clay; these were calculated for them by APEM, using the data provided in the final merged data tab. PSA_2111 recorded the highest percentage of gravel (90.79%) and the lowest percentage of sand (9.21%). This can be seen visually in Figure 2 and Figure 4. Inspection of the PSA_2111 raw sieve and laser data indicated that this discrepancy was due to a merging error; percentage laser data had been directly added to the sieve data (weight in grams) without being converted into weight. A check on the final merged data by calculating the percentage gravel, sand and silt/clay would have flagged up this error if it had been carried out prior to submission.

2.2.2.6 Fifty-forth distribution – PS54

There was good agreement for PS54 between the results from the analysis of replicates and those from the participating laboratories (see Figure 2). This was an artificially created sample using aggregate material and all laboratories only used dry sieving to analyse the sample. Table 3 shows the majority of participants recorded 100% gravel, the two that did not, recorded 99.96% (PSA_2101) and 99.98% (PSA_2108). The particle size ternary diagram in Figure 3 shows that all laboratories recorded that the sediment would be classified as Gravel. Figure 7b shows some of the z-scores for participants PSA_2108 and PSA_2109, are >1.96 between phi intervals 0.5 to 1.0 and 4.0 to 4.5phi. These laboratories followed different methods, sieving down to 63µm, and they therefore have small percentages of data in these phi categories that other laboratories did not record. PSA_2101 have a z-score of >1.96 for 0.5 to 0phi as they incorporated their sieve base-pan weight into this category. PSA_2110, PSA_2113 and PSA_2114 recorded the base-pan weight but did not incorporate it into their final merged data. However, in converting the weights into percentages they used the total weight from the sieve tab, therefore the final percentages do not equal 100%. PSA_2114 has a z-score of >1.96 in half-phi category -1.5 to -1.0; this is probably caused by a rounding error when converting weights into percentages (0.0084 has been rounded to 0.1 instead of 0.01). The main issue with exercise PS54 was whether or not to incorporate the base sieve pan weight into the final merged data. To clarify the sieve base pan weight should have been included in the final merged data in the 0.0 to 0.5 phi interval (707µm) or equally distributed across all size categories.

2.2.2.7 Fifty-fifth distribution – PS55

There was a fairly good agreement between the results from analysis of replicates and those from the participating laboratories (see Figure 2). All laboratories followed NMBAQC methods and used sieve and laser analysis apart from one (PSA_2109) who were following pipette methods as they do not own a laser sizer. Another laboratory (PSA_2111) stated they were following their own in-house method, but did not provide any details on this. The majority of laboratories following the NMBAQC method recorded similar quantities of sediment greater than and less than 1mm. Excluding PSA_2106, PSA_2109 and PSA_2111, the range of sediment weights >1mm was 71.13 grams and the range of sediment l <1mm was 20.44 grams. PSA_2106 appear to have filled in the sieve data tab incorrectly as they stated there was no material <1mm even though they used laser analysis. Based on evaluation of their raw data, it is possible their sieve data had already been converted into percentages in the sieve tab. Although their final merged data looked similar to other labs,

Table 1 in the interim report showed that PSA_2108 had only recorded a <1mm weight of 0.25g. Communication with the laboratory revealed that this was, as expected, a data entry error and the correct weight should have been 196.62g. This was rectified for the final report. PSA_2111 recorded a similar weight of >1mm sediment to other laboratories but their <1mm weight was considerably higher at 503.8 g; this resulted in a lower recording of gravel and higher recording of silt/clay compared to other laboratories. Communication following the interim report revealed that this was a wet weight rather than a dry weight and that the dry weight of the sample was approximately 200g.

The benchmark laboratory mentioned in the notes accompanying the re-analysis results that the sample was found to agglomerate in the laser analyser due to the large clay fraction, with runs 2 and 3 containing a progressively larger sand fraction than run 1: to prevent this, ultrasonics were used during sand loading and during the sample runs. This sample contained a small sand fraction in proportion to the silt and clay fractions; as a result, with the manufacturer's recommended obscuration settings of 8-12%, insufficient sand was added to the fluid module to be fully detected against the mud 'background'. Therefore, samples were run at 18-20% obscuration for the sand to be detected. Based on the laser metadata provided, most labs did use an obscuration higher than the manufacturer's guidelines.

2.2.3 Discussion

The samples distributed as PS52 appeared from an analysis of replicates (Figure 1) to be good replicates with very little variance. Results from participating laboratories (Figure 2) showed a general similarity in distribution curves, except for that of PSA_2107; who provided data that was a mix up between PS52 and PS53 for the interim report. They were subsequently sent spare replicates and repeated the exercises with a satisfactory result.

The samples distributed as PS53 appeared from an analysis of *replicates* (Figure 1) to be good replicates with little variance. The majority of results from participating laboratories were similar (Figure 2). PSA_2107 had the same issues with PS53 as with PS52, and they were sent a spare replicate PS53 sample to re-analyse, which was returned with a satisfactory result. PSA_2111 provided good raw sieve and laser data but did not merge these data correctly, resulting in the final merged data having a much higher percentage of gravel (Figure 4).

The samples distributed as PS54 appeared from an analysis of replicates (Figure 1) to be good replicates with little variance. Results from participating laboratories were in accordance (Figure 2). The main issue with exercise PS54 was whether or not to incorporate the base sieve pan weight into the final merged data. Three labs (PSA_2110, PSA_2113 and PSA_2114) did not include the base pan weight into the final data but divided by the total initial dried weight > 1mm to create percentages. This caused the final data not to equal 100%. The weights recorded in the base pan are only very small but can still have an impact. For example, by recording this small weight in the 0 to 0.5phi category has caused lab PSA_2101 to record a z-score greater than 1.96, suggesting that PSA_2101 were outliers when in fact they entered the data correctly, this shows another weakness in the z-score approach to comparing data.

The samples distributed as PS55 appeared from an analysis of replicates (Figure 1) to be good replicates with little variance. The majority of results from participating laboratories were similar (Figure 2). PSA_2111 was the main deviant by recording a much higher percentage of sediment <1mm. Subsequent communication revealed that this was due to the recorded weight being a wet weight rather than the dry weight specified for the NMBAQC methodology.

Participating laboratories were asked to provide a visual description of the PS52, PS53, PS54 and PS55 samples prior to analysis and instructed to describe the sediment using the Folk triangle post analysis, as well as to report the percentages of gravel, sand and silt/clay in each exercise. Data were provided by all but two (PSA2110 and PSA_2111) participating laboratories for PS52 and PS53, all laboratories for PS54 and all but one (PSA_2110) for PS55. APEM Ltd checked participants calculations using GRADISTAT based on the participants' final merged data. Of the data provided for PS52, all were correct apart from PS_2112, who provided data that was 1% out for sand and silt/clay. All data provided for PS53 and PS54 was correct. For PS55 two laboratories (PSA_2106 and PSA_2114) had summary statistics that differed from the APEM verification. However, these discrepancies were only small, 0.4% in both cases.

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 Scheme Year 21 a 'Pass' or 'Fail' flag will not be assigned to each lab for these particular exercises.

2.2.4.1 Laboratory Performance

Z-scores and cluster dendrogram figures are presented in each of the PS exercise reports; however these are only for illustration purposes. Investigations into new pass/fail standards have been completed using data from PS52 – 55. This review (Finbow & Hall, 2015) will be made available to view on the NMBQAC website. The new Pass/fail criteria using z-scores with robust statistics will be trialled in Scheme Year 22 (2015/16), the results of which will be reviewed in the next annual report

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

2.3.1 Description

The Particle Size Own Sample (PS-OS) module is a new module introduced in this scheme year (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 The PS-OS exercises will carry a pass/fail criteria however the 'Pass/Fail' flagging system introduced is a trial basis only and will not be used to asses the performance of a laboratory.

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 characteristics was to be recorded (pre-processing and post-processing using the Folk Triangle) along with the percentages of 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, expressed as a weight or 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.

2.3.2 Results

2.3.2.1 General comments

Eleven laboratories originally subscribed to the PS-OS module in 2014/15. Of these eleven, three pulled out and did not participate and four laboratories did not submit returns for any of the exercises. Of these four laboratories, one did not provide any explanation for their non-participation. The other three sets of PS-OS samples belonged to one participant who sub-contracted their work. A concerted effort was made by APEM, the contract manager Claire Mason and the participant to obtain the samples from the subcontractor. However, Year 22 was well under way before the matter could be resolved and it was decided that it was too late to now process the Year 21 samples. All labs involved now understand the PS-OS protocol and have submitted data sets and samples for Year 22.

Each laboratory received detailed comparisons of their data to the re-run by the NMBAQC Scheme's contractor along with a provisional pass/fail flag. Of the four laboratories that submitted data the correlation between the participant results and the NMBAQC Scheme contractor results were good. Based on the provisional pass/fail criteria being trialled, 91.6% of the samples would receive a Pass flag.

Labs generally provided workbooks with all the correct information. Three labs provided all necessary fractions of their sample for re-analysis. One lab (2103) did not provide any laser sub-sample, the < 1mm fraction for laser analysis was therefore reconstituted from the dried <1mm fraction. This caused these samples to have a slightly larger coefficient of variance; this was considered when comparing the samples.

2.3.2.2 Discussion

The PS-OS module raised issues over the interpretation of the methodology set out in the NMBAQC Best Practice Guidelines (Mason, 2015), in particular how the laser analysis is undertaken. These guidelines, 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 <1 mm in size. The methodology suggests 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, 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 instruments are calibrated properly and accuracy is checked in the normal way using standards and laboratory reference materials, and if samples are homogenised properly both before the sub-sample is taken from the bulk sample and when the representative sample is taken from the laser pot. In relatively rare instances where samples consist very largely of >1mm size material and it is impractical to obtain a representative test sub-sample for laser analysis from the bulk sample, more consistent laser results can be obtained by

taking a test sample from the wet separated <1mm fraction of the sediment, rather than from the bulk.

Where samples display, or are suspected of, unstable behaviour such as time-dependent agglomeration, repeat runs of the same laser test sample should be carried out. 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).

The returns for the PS-OS Year 21 module showed that some labs, particularly those using Coulter instruments, in routine case work usually only run one replicate through the laser, with replicates run every 20th or 50th sample. The results obtained by KPAL for the NMBAQC Year 21 replicates samples prepared by APEM 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.

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 weights provided. Raw laser data should be reported as volume percentages. (NB, following the conversion of sieve weights to weight percentages the data are merged with the volume percentages obtained from the laser analysis on the basis of weight proportions of the wet separated >1mm and <1mm fractions; merging of weight per cent and volume percent data introduces degree of error in the final merged data frequency distribution, but this is relatively small for most sample types).

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. Particle size exercises (PS) over the past twenty years have shown differences in the results obtained by different techniques (laser and sieve / pipette), in-house methods (*e.g.* pre-treatment) and also differences between equipment (*e.g.* Malvern Mastersizer 2000, Mastersizer X and Coulter LS230 lasers). The PS data also indicate that the variance between laser and sieve results is further emphasised by certain sediments characteristics, notably particle shape and density (Blott and Pye, 2006; Blott *et al*., 2004). The overall range of these variances needs to be determined if combining data sets derived from different methods. The NMBAQC's Best Practice Guide was developed for use in 2010/11 (Scheme Year 17); this has helped to reduce the amount of variation between methods. Sieve and laser metadata information sheets were added to workbook for 2014/15 to give more detailed information on methods used, particularly for laser analysis. It is essential that particle size data are presented with a clear description of the method of analysis and equipment used, including nature of any ultrasonic or other dispersion process, and the optical model values which have been assumed.

4. An improved learning structure to the Scheme through detailed individual exercise reports has been successfully implemented and was continued in this Scheme year. For the PS exercises, detailed results have been forwarded to each participating laboratory as soon after the exercise deadlines as practicable. Participants who submitted significantly incorrect data were contacted immediately to ensure that in-house checks can be implemented to ensure future quality assurance. The PS52, PS53, PS54 and PS55 reports included the data submission sheets received from all participants as an appendix; Participants are encouraged to review their exercise reports and provide feedback concerning content and format wherever appropriate.

5. The current NMBAQC Scheme standards for PSA are under review. The alternative use of z-scores for each phi-interval, trialled in Scheme Year 17 appears 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 data

submitted by the majority of respondents are broadly correct; the fact that this is not always the case raises genuine concerns regarding technique and method bias. Alternative flagging criteria using z-scores descriptive statistics combined with robust statistics have been reviewed during the current year and will used to inform quality assessment procedures in future years.

6. The Year 21 PS-OS module highlighted differences in methodology between laboratories, particularly in the creation of laser data (at those laboratories where laser diffraction is used). Some labs clearly use methods that vary substantially from those described in the NMBAQC's Best Practice Guide. In view of the results obtained from the Year 21 PSA exercises, and from parallel experimental work undertaken by the NMBAQC QC analytical contractor, the need has been identified for certain aspects of the Guidance to be clarified and modified. It is intended that these amendments to the Guidance will be published shortly. It has been suggested by KPAL that, for the vast majority of samples, the accuracy of reported results does not increase greatly with analysis multiple replicates and averaging of the data obtained, provided that appropriate guidelines for sample mixing, sub-sampling and dispersion are followed, and that perhaps the guidance should be updated to reflect this.

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