Standard Operating Procedure for:

Quality Assurance/Quality Control and Data Review/Authorization in the GC-Pesticides/BNA Laboratory

DEPARTMENT OF ENVIRONMENTAL PROTECTION
CHEMISTRY SECTION
TALLAHASSEE FLORIDA

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1. SCOPE AND APPLICATION

1.1. This SOP details the Quality Assurance (QA) and Quality Control (QC) procedures for the GC-Pesticides/BNA Work Group. It also outlines the data review/authorization procedure followed by the Group.

1.2. Quality Assurance consists of all of the practices undertaken in a laboratory to ensure the data generated are as accurate and precise as possible. QA includes general quality control measures as well as specifics protocols such as the cleaning of glassware and preparation of standards. This SOP will concentrate on Quality Control measurements that are used to measure and track the Quality Assurance in the GC-Pesticides/BNA laboratory. It will touch briefly on some general guidelines for QA. Refer to the individual preparation or analysis SOPs for more specific details on QA.

1.3. Most of the QA/QC and the data review/authorization practices described here are common throughout the Chemistry Section.

2. DEFINITIONS

2.1. The quality control measurements used in the GC lab are Accuracy, Precision, Blank Evaluation and Detection Limits (method detection and practical quantitation limits-MDL/PQL). These are briefly defined as follows:

2.2. Accuracy is the term which describes the degree of deviation (bias) between a known amount of analyte added to a sample and the actual recovery amount of the analyte. It is expressed as the percent recovery.

2.3. Precision is the term which describes the degree of replication between duplicate samples. It is calculated and expressed as the Relative Percent Difference (RPD) between duplicate sample results.

2.4. Blank Evaluation is used to assess the degree of contamination resulting from the sample preparation and analysis steps.

2.5. Detection limits (MDL/PQL) are established during the validation of a method. These limits define the sensitivity of a method. Because "zero" has no meaning when an analyte is not detected, a method analyte must have a limit set which defines the lowest concentration that can be reliably seen when it is detected.

2.5.1. Method Detection Limit (MDL/LOD): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is also referred to as the Limit of Detection (LOD).

2.5.2. Practical Quantitation Limit (PQL/LOQ): Usually set at 3-5 times the MDL, it is a more reliable measurement limit. Although the MDL can be detected at a 99% confidence, the PQL is usually the point where the analyte can be quantitated more accurately. The PQL is also referred to as the Limit of Quantitation (LOQ).

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3. INTERNAL QUALITY CONTROL SAMPLES

3.1. For every batch of 20 samples, the following quality control samples are prepared and analyzed:

3.2. One or two Method Blanks (MBLK; used to evaluate contamination in the laboratory)

3.2.1. These are reagent blanks that are treated exactly as samples, including exposure to all glassware, equipment, solvents and reagents used with other samples. The lab blank is used to determine if the method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.2.2. If the Method Blank is found to be contaminated, the source of contamination must be found and eliminated. All the affected samples, that are within holding times, must be re-extracted, and re-analyzed. The affected samples are the ones where the same positive(s) was found up to ten times the result in the blank. If samples passed the holding time, the results will be reported with a "V" qualifier (ref 9.3) up to ten times the amount found in the blank.

3.3. Laboratory Control Samples (LCS and LCSD aka LFBs)

3.3.1. An LCS is a reagent blank that is fortified at sample extraction with a known amount of the analyte(s) of interest and with any surrogates used.

3.3.2. LCSs are used to assess the method accuracy (i.e., analyte percent recovery) without the effects that a true sample matrix may contribute. If prepared in duplicate, it is also used to assess method precision (as Relative Percent Difference, RPD).

3.4. Matrix Spike Samples (for assessing method accuracy and, if performed in duplicate, for assessing precision on "real" samples, in the presence of matrix effects.)

3.4.1. Matrix Spike Samples are samples that are fortified at sample extraction with a known amount of an analyte(s) of interest.

3.4.2. Every attempt is made to prepare Matrix Spikes in duplicate, to assess the true method precision in the presence of matrix effects. Spike recoveries (accuracy) are indicators of sample matrix interference, loss of analyte and contamination. Historical percent recoveries are used to calculate method bias and the confidence range of the bias. If insufficient sample is available to prepare matrix spikes in duplicate, LFBs precision has to be used to assess method precision.

3.5. Spiking Policy

3.5.1. All analytes included in the test are spiked in both LFBs and Matrix spikes.

3.5.2. For PCB aroclors a mix of PCB-1016 and PCB 1260 (called PCB 1060) is routinely spiked. It covers the entire PCB range. Other PCB aroclors are only spiked on request from customers.

3.6. Other Quality Control measures that may be used are:

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3.6.1. Instrument Blank (a solvent injection on the GC, to assess presence of possible instrument contaminants). In the event a positive identification is found in both the sample(s) and the instrument blank, the instrument must be cleaned and the sample rerun/reanalyzed.

3.6.2. Internal Standard - a pure analyte(s) of known amount that is added to the final sample extract prior to GC analysis. It is used to measure the relative response of other analytes and surrogates and is useful in correcting for injection variations. It is also used as a retention time reference peak, to correct for retention time drift during an analysis sequence. The internal standard must be an analyte that is not expected to be found in the sample.

3.6.3. Surrogate- a pure analyte(s) that is added to all samples, blanks and spikes before extraction. Surrogates should be similar in behavior to the method analytes but SHOULD NOT be expected to appear in the sample. Surrogate recoveries give an indication of method accuracy and are a good check for gross inaccuracy (i.e., lost sample, incorrect volumes, concentration problems, etc.) in all the samples.

4. EXTERNAL QUALITY CONTROL SAMPLES

4.1. There are field QC samples that are assessed along with the samples. These are:

4.1.1. Field Duplicate Samples- two separate samples collected at the same time and from the same site under identical circumstances and treated the same through all field and lab procedures. Duplicate analyses give a measure of the precision associated with the sample collection, preservation, and storage, as well as with the laboratory procedures.

4.1.2 Field Blank - reagent water added to a sample bottle at the time of sample collection. It is treated exactly as a sample, including exposure to the sampling site conditions, storage, preservation, and all laboratory procedures. It is used to determine if method analytes and/or other interferences are present in the field environment. In case a positive identification is found in a field blank, but method blank(s) pass, all field blank detections above PQL generally need to be confirmed by re-extraction. If the field blank detections are below PQL, then the re-extraction is not necessary in the following cases:

- The same analyte is not found in the associated samples (samples in the same job),
- The same analyte is found in the associated samples at levels at least 10 times the value in the field blank.
- It is always prudent to confirm the results in extract by rerun, before sending the field blank for re-extraction. The above rules also apply to samples with matrix “DI water” even if they are not specifically called field blanks.

4.1.3. Equipment Blank - After sampling, the equipment (baler, etc.) is rinsed with reagent water and collected as a sample. This blank is evaluated to ensure that the field equipment did not contaminate the samples. In case positive hits are detected in the equipment blanks, rules similar to 4.1.2 are to be followed. One needs to be aware that equipment blanks are frequently associated with soil samples.

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4.1.4. Trip Blank - This is generally used only when sampling for volatile organic compounds. A trip blank is prepared in the lab by filling up the sample bottle with reagent water and sending the filled, capped bottle out to the collection site with the other associated sample bottles. The trip blanks go on the entire sampling "trip", so they are exposed to all aspects of the sampling collection, storage and transportation. The trip blank sample bottle remains closed at all times, and is used to determine if any method analytes or interferences have diffused into the sample bottle through its bottle cap. In case a positive identification is found in the trip blank procedure from 4.1.2. has to be followed.

4.1.5. Field Spikes - These can be matrix or reagent water fortified samples that are used to assess the stability and method performance of an analyte(s). These may be "blind" spikes, which are not labelled as spikes and are therefore unknown to the laboratory personnel. This is an excellent way to determine true method performance.

5. QC CALCULATIONS/REPORTING CONVENTIONS

5.1. Accuracy (expressed as % Recovery) of LFBs and matrix spikes is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Measured conc. of Spike} - \text{Measured conc. in unspiked sample}}{\text{True Value}} \times 100$$

5.2. Precision (as Relative Percent Difference-RPD of the measured recovered concentration of duplicate LFBs and matrix spikes, or RPD of duplicate sample results) is calculated as follows:

$$\text{RPD} = \frac{|A - B|}{(A + B)} \times 2 \times 100\%$$

where:

A = measured concentration of spike 1 (or sample concentration from sample 1)

B = measured concentration of spike 2 (or sample concentration from sample 2)

Note that this value is the Difference between the measured recovered concentrations from samples A and B, divided by the Average of the 2 values.

5.3. Acceptance Limits for accuracy and precision are established by evaluating Matrix Spike / LFB recoveries. These limits are used in assessing the acceptability of subsequent accuracy/precision of a spike and in determining if the value is a true and accurate reflection of the method performance. Limits are established for each matrix (i.e., sediment, water, tissue). Statistical recovery limits for LFB/MS and surrogate recoveries are typically based on the QC Manager statistics for the last two calendar years (if available; it may be more than two years- up to five if necessary). The limits are recalculated, at least annually. The results of statistical calculations are saved at FLDEP1\DATA\DEAR\LABS\LAB5\CHEMISTRY\ORGANIC\QC LIMITS STATS. The statistical recovery limits are then entered into QC Manager limits tables (an automatic update function exists for this operation within QC Manager). The initial QC limits are replaced with statistical ones whenever enough data points are accumulated. At least 20 points are required, but it is preferable to wait for about 50 points or more. If enough data

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points are available for LFBs but not for matrix spikes, then LFB statistical limits may be applicable for both categories on temporary basis.

5.3.1. Accuracy Acceptance Limits consist of both Warning Limits and Control Limits:

5.3.1.1. Warning Limits are based on 95% confidence level. This calculation will give an upper and a lower warning limit for the accuracy values. Warning Limits are used in evaluating data trends.

Upper Warning Limit (UWL) = Mean + $t_{(0.95)}$ Sd
Lower Warning Limit (LWL) = Mean - $t_{(0.95)}$ Sd

5.3.1.2. Control Limits are based on 99% confidence interval level. This calculation will give an upper and a lower control limit for the accuracy values.
Upper Control Limit (UCL) = Mean + $t_{(0.99)}$ Sd
Lower Control Limit (LCL) = Mean - $t_{(0.99)}$ Sd

Where:

- Sd is the standard deviation of the population.
- Mean is the average of all points.
- $t_{(0.99)}$, $t_{(0.95)}$ are the Student's coefficients for two-sided statistics for 99% and 95% confidence intervals respectively.

Lower Control Limits should not be set to less than 10% for LFBs and Matrix Spikes, and less than 20% for surrogates. Upper control limits should not be set to more than 250% for LFBs and surrogates and more than 300% for Matrix spikes.

5.3.2. Precision Acceptance Limit

5.3.2.1. Warning and Control Limits are based on a 95% and 99% confidence levels, respectively. For precision, only the upper limits are relevant.

Upper Warning Limit (UWL) = Mean + $t_{(0.95)}$ Sd Upper Control limit (UCL) = Mean + $t_{(0.99)}$ Sd

Where:

- Sd is the standard deviation of the population.
- Mean is the average of all points.
- $t_{(0.99)}$, $t_{(0.95)}$ are the Student's coefficients for one-sided statistics for 99% and 95% confidence intervals respectively.

Upper control limits for precision should not be set to more than 100%. For some analysis in GC group statutory control limits for precision of <30% may be used. It may take a very long time, for seldom performed tests, to acquire enough data points to perform statistical calculations.

Statistics for some analytes may not follow the normal (Gaussian) distribution model. They are skewed. Skewness becomes apparent when failure rate is calculated based on the limits obtained for assumed normal distribution. If that failure rate is much higher than expected 1%, then the statistics for the affected analytes may be recalculated using a "non-parametric" ranking model. A minimum of 200 points for accuracies and 100 points for precisions is necessary for this approach.

5.3.3. For failing analytes, the results must be qualified according to Lab SOP **LB-027**. In addition, a comment is added to the LIMS report detailing the outlier data.

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5.3.4. If 20% or more analytes in the tests (for multiple component tests) have LFB failures the entire batch is considered to be out of control and needs to be re-extracted, and the re-extraction data has to be reported.

5.3.5. If consistent deviations from QC limits, deemed to be caused by systematic errors of the procedure, are observed in LCS recoveries/precision, the analyst must proceed with 5.3.5.1 and 5.3.5.2

5.3.5.1. Locate and correct the source of the problem.

5.3.5.2. Repeat the test for all parameters that failed to meet the criteria.

5.3.6. Repeated failure, however, will indicate a general problem with the measurement system. If this occurs, repeat 5.3.5.1. and 5.3.5.1. until the problem is solved.

5.3.7. For qualifying data in case of LCS failure due to a Systematic Error, see Laboratory SOP **LB-027** Footnote 4 (See Ref. 9.3).

5.4. Rounding of Numbers

5.4.1. For rounding of numbers follow the Laboratory SOP **LB-024** (See Ref. 9.2). For all reported data, round results to 2 significant figures.

5.5. LIMS Reporting Codes/Conventions (ref 9.6)

5.5.1. Samples that are analyzed after expiration must be reported with a qualifier (Q).

5.5.2. For sample results that are below the MDL report the MDL followed by the letter U.

5.5.3. For sample results that are below the PQL but above the MDL, report the sample result followed by the letter I.

5.5.4. For samples that are analyzed in duplicate (in-lab duplicates, NOT field duplicates) report the average of the results followed by the letter A.

5.5.5. For data that are reported as positives but are below MDL the reported value must be followed by the letter T.

5.5.6. For some other conditions that require using qualifiers follow the rules in Laboratory SOP **LB-027** (see Ref. 9.3).

5.5.7. Report all water and TCLP/SPLP results in ug/L or ng/L (based on specific test), all sediment, tissue and waste samples in ug/kg. Sediment samples are reported on dry weight basis, while tissue and waste samples on wet weight basis.

6. MDL/PQL DETERMINATION/METHOD VALIDATION

6.1. MDL and PQL values are initially determined during validation of a new method and must be verified at least once per year or every time significant changes were made in the procedure.

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6.2. MDL calculation use EPA's recommended method (40 CFR pt. 136 Appendix B, see Ref. 9.5)

6.2.1. Estimate the MDL by analyzing a set of standards on the appropriate instrument and examining the chromatographic peak. The peak should at least have signal to noise ratio (S/N) of 5.

6.2.2. Once the estimated MDL is available, at least 7 replicate spikes and at least seven replicate blanks are prepared in, at least, three batches on three separate days. Laboratory pure water, Ottawa sand or other pure matrix is used and the spiking level is generally about 2-4 times of the estimated MDL. These spikes and blanks are then analyzed on all instruments considered identical for the purpose of the specific analysis. At least two spikes and two blanks are run on each instrument. The standard deviation and relative standard deviation for the measurements are calculated. The relative standard deviation should be acceptable, based on EPA method or other references results (usually less than 30%). The MDL is calculated using these formulas:

$MDL = t \times s$ for spikes
$MDL = avg + t \times s$ for blanks

where: t is the Student coefficient for 99% confidence level one-sided statistics and n-1 degrees of freedom. "n" stands for the number of replicate samples. "s" is the standard deviation, and "avg" is the average blank value.

6.2.3. The reported MDL must be set at the highest of the two calculated MDLs (spikes and blanks). It may be further elevated to address real world matrices.

6.2.4. The PQL is set usually at 3-5 times the MDL. The same spikes are usually used as MDL and PQL verifications. However, in some cases they may need to be separated, and another, higher, spike used for PQL verification.

6.3. These MDLs and PQLs are used when reporting data. However, these MDL/PQL values may be adjusted when analyzing real samples, to account for differences in matrix interferences, sample wet/dry weight and amount of sample analyzed.

7. QUALITY ASSURANCE

7.1. The following are general guidelines to use in assuring good and complete data are reported. This is not a complete list of guidelines!

7.2. All data and quality control data are reviewed by a supervisor before being accepted as final.

7.3. All maintenance or analytical problems are reported to a supervisor.

7.4. Field sampling problems such as contamination, labeling, and holding times are reported to a supervisor and noted with the results.

7.5. Document quality control from all analysis sets at it is established in LIMS.

7.6. Document QC deviations in the final LIMS report by adding appropriate comments and by flagging any affected results with the proper code.

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7.7. Method interferences may be caused by contaminants in reagents, glassware, instrumentation, and highly contaminated samples. All these contaminants must be routinely monitored by analysis of sample preparation blanks. To avoid method interferences, take the following general precautions:

7.7.1. Solvents

7.7.1.1. Always use only the specified grade of solvents. If interferences from solvents are suspected, analyze a concentrated aliquot of the solvent to check this. Remove any contaminated solvent from production IMMEDIATELY. Label solvents as contaminated and dispose.

7.7.1.2. Never use solvents from unlabeled bottles.

7.7.1.3. Never pipet solvents directly from bulk solvent. Always transfer the required volume of solvent to a labelled beaker and pipet from this. Dispose of the unused portion.

7.7.2. Reagents

7.7.2.1. Use the purity of reagents recommended by the appropriate SOP.

7.7.2.2. Store all the reagents appropriately in a clean environment, and with a proper label, which includes the date and initials of the person who prepared the reagent.

7.7.3. Use scrupulously cleaned and checked glassware. See Lab SOP **CM-031** (ref. 9.4) for details.

7.8. BE SENSITIVE TO CONTAMINATION AT ALL TIMES! If a highly contaminated sample has been analyzed with other non-contaminated samples, be sure that any positives reported in the other samples are true! Positive results seen in other samples may be carry-over from this highly contaminated sample. It is imperative to frequently clean/replace all the vials on the autosampler turret and replace the diffusion caps on the solvent vials whenever they become dirty. The waste vials on the turret must be emptied frequently and never allowed to go above the half-way line!

8. DATA REVIEW AUTHORIZATION CHECKLIST

Before any test can be authorized the supervisor (or designate) must conduct a thorough review of the entire data package and the upload process and then affix their signature and date of review to all data packs. The signature of the supervisor indicates that the appropriate data review checks indicated below were performed on the date indicated.

8.1 **Sample Preparation** (primary responsible party: GC group supervisor, but the analyst involved in the data processing must also review to provide a secondary check)

- Review sample preparation records and verify that the correct preparation was used for the samples. If not, re-prepare using correct method.

- Verify appropriate matrix spike and surrogate solutions were used (were correct levels/solutions used? check expiration date of solutions). If solutions have expired, samples must be re-prepared, or data must be flagged appropriately with a “J”.

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- Verify preparation holding times were met - if not, flag data appropriately (i.e., LIMS will append "Q" qualifier to all reported data).

- Note any observations made by the sample prep team (e.g., unusual odors, colors, reaction during prep); consider these in making any determinations.

- Ensure that appropriate QC samples were prepared/analyzed for the sample batch (e.g., blanks, LFBs and duplicate matrix spikes per batch of 20, etc.) - if not, re-prepare samples if there is sufficient time remaining prior to sample expiration. If there is insufficient time prior to expiration, continue with analysis but flag data with the "J" qualifier.

8.2 **Instrumental Analysis** (primary responsible party: analyst). The supervisor of the work group, or another senior analyst provides a duplicate check of the same items).

- Ensure that a valid initial calibration for all parameters analyzed is on file and complies with method specifications. If not, re-analyze sample batch after generating a valid initial calibration curve. If samples have already passed the analysis holding time of 40 days, report data flagged with the qualifier "J". Include comment in final report explaining the use of this qualifier.

- Ensure that passing continuing calibration verification (CCV) standards for all parameters reported has been analyzed every analysis run sequence and complies with method specifications**-**. If CCVs do not meet method requirements but the associated analytical results are below the detection limit or below the quantifiable threshold (PQL) and no systematic failure is observed (i.e., the failure is deduced to be due to a statistical outlier in a multi-component analysis where results from other CCV components and LFB results do not indicate a systematic bias in the analysis or detector response), an appropriate test comment and result qualifier (J) shall be provided to indicate the CCVs are outside control limits. However, when a systematic or system failure is detected or the affected analytical data are above the quantifiable threshold, the analysis shall be re-run if possible. If re-analysis is not an option, the analytical results shall be qualified as estimates.

- Check if the tune check for the GC/MS/MS analysis was performed and whether it passed.

- Check surrogates, lab fortified blanks and matrix spikes for recoveries/precision (if applicable). Ensure that all are within the current QC acceptance range. If they are outside acceptance ranges, a comment must be included in the report and data is qualified accordingly (i.e., append "J" qualifier to all reported positive hits. Include comment in final report explaining the use of this qualifier). See also DEP SOP LB-027.
- Check internal standard (ISTD) area counts. Confirm that they comply with method specifications. If ISTD response is outside of acceptance limits (typically -50-+200%), re-analyze sample to determine if the sample injection was faulty. If the ISTD response is still outside control limits, flag the positive hits above PQL with qualifier "J" and include comment.

- Ensure that any retention time drifts are within method specifications**;** if not, re-analyze sample batch after performing any necessary instrument maintenance (e.g., check for leaks, check injector function). Compare the RT shifts with the shifts of internal standards. If they are similar, it indicates matrix induced effects. If the RT shifts are caused by heavy matrix, then diluting the sample will reduce the shift. If the RT shift is not affected by dilution, the positive is not real and it needs to be dismissed. In some cases, it may be necessary to report data flagged with the qualifier "N". Include comment in final report explaining the use of this qualifier.

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- Check tailing factor /DDT-p,p' decomposition reports for for GC/MS/MS and GC/MS analysis. Tailing factor for Pentachlorophenol may not be above 2.0 and the DDT-p,p' degradation cannot exceed 20%. Clean the instrument and rerun the samples if failures observed. If samples are expired, flag the positive hits with qualifier "J" and include the appropriate comment.

- Check field duplicates/replicates: is the degree of precision within accepted margins? -If not, re-analyze duplicates/replicates samples. Include the appropriate comment in the final report if precision is outside accepted limits.

- Check laboratory, trip, field and/or equipment blanks for evidence of laboratory or field contamination. If laboratory contamination is suspected, delineate whether the contamination occurred at prep or analysis step - it may be possible to re-analyze or re-prep batch, if samples have not exceeded their holding time. If a sample batch must be reported that has an associated method blank contamination, the affected samples' results will be reported with a "V" qualifier up to ten times the amount found in the blank.

- For positive hits, check the integration of the peak to ensure that the baseline was drawn appropriately. Use manual integration to correct the baseline if needed. Ensure that this technique was utilized appropriately based on lab accepted protocol (See Lab SOP CM-018-1. Ref 9.7). If a parameter cannot be accurately quantified due to matrix interferences, the result for the affected parameter must be flagged as an estimate (i.e., append the qualifier "J" to the final result). Include comment in final report explaining the use of this qualifier.

- Two criteria must be satisfied to verify identification of a compound by GC/MS/MS, GC/MS SIM, GC/MS full scan, or GC/MS NCI: 1.) elution of the sample component at the same GC retention time window as the standard component: and 2.) the relative ratios of qualifier to quantifier ions has to pass the method criteria.

  If any samples contain parameters at concentrations higher than the calibration range, ensure that they were properly diluted and re-analyzed. If sample was not diluted within the calibration range, prepare the appropriate dilution and re-analyze. If the sample extract has exceeded its holding time, report result but append the qualifier "J".

- Review all sample calculations- ensure any dilution factors and dry weight corrections were properly applied. Make corrections as needed.

- Ensure appropriate qualifiers are used. Refer to the DEP SOP LB-027. for details on the use and the reporting priority of these qualifiers.

- Check all information in the Analysis Summary Report Header (SOP number, Instrument ID, Column ID) to be right. Make correction as needed. Also verify that all run sequences, including reruns, are included in the analysis file**.**

- Evaluate data against any field information. Do the results make sense, given the field information? For example, does the trip blank contain several hits while an effluent sample does not? If anything looks suspicious, further research is necessary before posting results. Ensure that these guidelines were properly followed.

- Check NCR report in the Laboratory Information Management System (LIMS) Data Review/Authorize for field preservation records (e.g., log-in details and sample prep records) for any indication that samples were improperly preserved at collection. If samples were received improperly preserved) sample held at temperatures > 6 deg. C), all data must be flagged with a "Y".

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8.3 QCM review.

- Check if a proper code is applied to surrogates. If in doubt, check with the supervisor.
- Check if a correct matrix is applied to samples and LFBs.
- Check if correct preconcentration factors are used, including QC samples.
- Check if correct sample weights/ dry weights are used (for soils).
- Check if correct dilution factors are applied. Dilution factors should not be applied in Masshunter!

8.4 **Uploaded LIMS Data** (primary responsible party: analyst, work group supervisor. The Environmental Administrator of the work group provides a secondary check for the items noted by *)

- Compare effluents with backgrounds - usually effluent concentrations will be higher than background concentrations *
- Compare results with any information known about the site, i.e., are the reported hits consistent with what is known about the site history? *
- Confirm sample prep dates and analysis dates are correct (e.g., does prep come BEFORE analysis?) *
- Make sure the result has the correct number of significant figures. *
- Ensure appropriate qualifiers are used and that comments are entered when needed (i.e. confirmation of blank contamination etc.). *
- Verify that sample identifier information in the LIMS matches that in the reported data package.
- Evaluate data against any field information. Do the results make sense, given the field information? For example, does the field blank contain several hits while an effluent sample does not? If anything looks suspicious, further research is necessary before posting results. *

For additional details, refer to internal GC SOPs.

8.5 Test Level Authorization of Data Review (primary responsible party: work group supervisor or designate)

After completion of the above data review process, the supervisor (or designate) must affix their signature and date of review to the data package. This signature and date indicate that the above checks were performed on the date indicated. If any check results in a corrective action(s), the supervisor (or designate) must indicate the corrective action(s) performed and affix their signature and date, indicating that the specified corrective action was initiated and completed satisfactorily.

8.6 Sample Level Authorization.

- Perform calculations on all tests at once. Make sure the correct number of surrogates is reported.
- Add calculation comments for failing surrogates and method blanks.

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- Review the QC data. Make sure the NCRs are present and authorized whenever the number of LFB failures exceeds the acceptable marginal exceedances. See appendix A
- Make sure that NCRs are created and authorized for CCV failures. See appendix A
- Check for other NCRs (like improper preservation) and make sure data is properly qualified and commented.
- For "cracked cap" NCRs make sure that the unaffected container was used, and a comment was provided.
- Make sure the data is properly qualified and commented.
- Make sure the MDLs (non-detects) make sense when compared to MBLK data.
- Review the positives for all tests. Make sure they make sense against field information, like blanks, duplicates, customer spikes, pre, mid and post filters, etc.
- Compare chlordane results to those for specific individual chlordane components: alpha and gamma chlordanes and cis and trans nonachlors. Typically, the sum of the four components should be less than half of the chlordane concentration, and it can never be higher than chlordane concentration!

9. REFERENCES

9.1. 2016 TNI Standard, Volume 1, Module 4.

9.2. DEP SOP LB-024, Significant *Figures: Policy of the DEP Bureau of Laboratories.*

9.3. DEP SOP LB-027, Reporting *Qualified Data and Correcting Quality Control Problems.*

9.4. DEP SOP CM-031, Glassware *Cleaning and Muffle Furnace Protocols in the Organic Preparations Laboratory*.

9.5. C.F.R. Appendix B to Part 136. Definition and Procedure for the Determination of the Method Detection Limit..

9.6. Chapter 62-160, Florida Administrative Code.

9.7. DEP SOP CM-018, *Laboratory Policy Regarding Manual Chromatographic Peak Integration.*

10. APPENDICES

10.1 Number of allowable marginal exceedances for LFB and CCV

number of analytes in LFB or CCV	number of allowable exceedances	tests
>90	5	W-BNA-R, S-BNA, W-BNA
71-90	4	W-PSNP-TQ
51-70	3	S-PSNP-TQ
31-50	2	W-PCL-TQ-R, S-PSCL-TQ
11-30	1	W-TR-SQ-R
1-10	0	all FL-pRO, PCB and CT-CI tests

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10.2 Analysis of TCLP/SPLP samples.

TCLP/SPLP extractions are currently performed by the Metals group and the prep worksheets are created and completed at that stage. The status is also changed to "V" at that time. The TCLP/SPLP extracts are collected in 500 mL glass amber bottles and delivered to the GC Prep Laboratory where they are stored in a sample refrigerator. A TCLP/SPLP blank for each batch is also included. The samples are then treated and analyzed as regular water samples as per appropriate test. However, an electronic worksheet cannot be created as the status is already "V". Samples must be extracted by GC prep staff within seven days of submission by the Metals group. Samples, and the TCLP/SPLP blank, are extracted with usual water extractions' set of QC samples including MBLK, LFB and MSs. The extraction details are recorded by the staff members. When two TCLP/SPLP batches are combined into one GC batch the associated QC will have to be reported twice with the two prep batch ID numbers. TCLP blanks are considered additional MBLKs and trigger the same reporting rules if failures are encountered.

APPENDIX OF SIGNIFICANT CHANGES

04/12/2016 Section 3.2.2; raising the detection limit discussed, application of the "V" qualifier added with reference to chapter 62-160, FAC (FDEP response to CERP audit, section 6a)

Section 5.3; calculation and application of recovery limits for LFBs and Matrix spikes clarified. (FDEP response to CERP audit, section 6b)

Reference 8.6 to Chapter 62-160 FAC added (FDEP response to CERP audit, section 6c)

Section 5.5.7 expanded to indicate that sediment samples are reported on dry weight basis, while tissue and waste sample on wet weight basis. (FDEP response to CERP audit, section 6d)

04/06/2017 QC calculations for recovery limits explained in details.

04/04/2018 Data review/authorization checklist SOP OG-003-2.19 merged with this SOP. MDL procedure updated. Added Table of Contents.

3/16/2020 Removed requirement specific to GC-ECD technology that is no longer in use.

12/20/2021 Updated recovery/precision statistics section including nonnormal distributions. Added sample level authorization chapter. Removed references to GC-NPD/ECD methods including spike rotation procedures. Field blank re-extraction rules added.

12/08/2022 Re-extraction rules for equipment blanks and method blanks clarified.

11/02/2023 Editorial changes throughout the text.

10/21/2024 BNA analysis included. Updated re-extraction rules for field blanks. Appendix 10.1 added specifying the number of allowable exceedances for CCVs and LFBs. QCM review chapter added.

10/27/2025 Added Addendum 10.2 describing analysis of TCLP/SPLP extracts.

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