Standard Operating Procedure for:

ANALYSIS OF PESTICIDES AND PCBs IN WATER, SOIL AND TISSUE SAMPLES USING GC/MS/MS

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CONTENTS

1. SCOPE AND APPLICATION

2. SUMMARY OF THE METHOD

3. INTERFERENCES

4. DEFINITIONS

5. APPARATUS AND EQUIPMENT

    5.1. Apparatus
    5.2. Data System
    5.3. Gases

6. REAGENTS AND CHEMICALS

    6.1. Solvents
    6.2. Standards
    6.3. Stock and intermediate standards
    6.4. Working standard solutions
    6.5. Spiking Solutions
    6.6. Initial Calibration Verification (ICV)
    6.7. Continuous Calibration Verification (CCV)
    6.8 Analyte protectants

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8. SAMPLE PREPARATION PROCEDURE

9. GENERAL DESCRIPTION OF GC/MS/MS ANALYSIS

    9.1 GC/MS/MS Maintenance and Tuning
    9.2 GC/MS/MS system Initial Calibration
    9.3 Daily GC/MS/MS Performance and Calibration Check
    9.4 GC/MS/MS Sample Analysis
    9.5 Data processing using the Masshunter software

10. REPORTING AND DOCUMENTATION

11. QUALITY CONTROL

12. DATA ARCHIVAL

13. DETERMINATION OF METHOD DETECTION LIMITS

14. SAFETY

15. REFERENCES

16. TABLES

17. APPENDICES

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of selected organonitrogen and organophosphorus pesticides in water samples as listed in Table 1A, selected organochlorine pesticides in soil as listed in Table 1B and in water (Dieldrin only) as listed in Table 1E, PCB Aroclors in soil as listed in table 1C, and selected organochlorine pesticides and PCB congeners in fish tissues as listed in table 1D. Method Detection Limits and Practical Quantitation Limits yielded by this method are also provided in Tables 1A, 1B, 1C, 1D and 1E.

1.2. This method is based on EPA 8270D mod. (ref 15.1) Laboratory Information Management System (LIMS) tests: W-PSNP-TQ, W-DIELDRIN, S-PSCL-TQ, S-PCB-TQ, WS-PSCL-TQ, WS-PCB-TQ, S-PSNP-TQ, WS-PSNP-TQ, T-PCBCL-TQ and T-PCB-TQ.

1.3. This Standard Operation Procedure is restricted to use by an analyst experienced in the use of an Agilent 7000C or 7010 GC/MS/MS triple quadrupole system, and in the use of appropriate computer programs. The minimum qualifications required:

- B.S. in Chemistry or Biochemistry with minimum one year of professional chemical or biochemical experience
- Knowledge of principles and practice of gas chromatography/mass spectrometry
- Ability to perform basic laboratory mathematics
- Knowledge of the Masshunter GC/MS/MS software and DEP LIMS.

2. SUMMARY OF THE METHOD

Water and soil samples are extracted using the appropriate procedures listed in the Preparation SOP- GC-002 (ref 15-2). Water samples for W_DIELDRIN test are prepared by Solid Phase Extraction as described in DEP SOP GC-036-1 Tissue samples are extracted according to preparation SOP GC-004-1. (ref 15-16). The extract is analyzed using an Agilent 7000C or 7010 GC/MS/MS triple quadrupole system operating in the Multiple Reaction Monitoring (MRM) mode. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of the characteristic MRM transitions. Quantitative analysis is performed using an internal standard technique.

3. INTERFERENCES

3.1. Raw GC/MS/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2. Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. To reduce carryover, rinse the syringe several times with solvent between samples. It may be necessary to analyze one or more solvent blanks between samples and even change out the syringe in extreme cases.

3.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must routinely demonstrate to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by rinsing with DI water. The glassware should then be drained dry, and heated in a muffle furnace at 550 °C for

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8 hours. Some thermally stable materials may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may supplement the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required or irradiation with UV light. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the sample characteristics.

4. DEFINITIONS

4.1. ACCURACY: The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

4.2. BATCH: A group of samples, which behave similarly with respect to the sampling or the testing procedures being employed, that are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

4.3. BIAS: The deviation due to matrix effects of the measured value (Xs - Xu) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (Xs - Xu) - K$$

where:
Xs = measured value for spiked sample,
Xu = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100\ (Xs - Xu) / K$$

4.4. PRACTICAL QUANTITATION LIMIT (PQL): The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is generally 3 to 5 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the PQL concentration is selected as the lowest non-zero standard in the calibration curve. Sample PQLs are highly matrix-dependent.

4.5. FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

4.6. INTERNAL STANDARD: A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

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4.7. LABORATORY FORTIFIED BLANK/LABORATORY CONTROL SAMPLE (LFB/LCS): A known matrix material spiked with compound(s) representative of the target analytes. The LFB is analyzed exactly the same way like other sample. This is used to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

4.8. MATRIX: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

4.9. MATRIX SPIKE: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

4.10. MATRIX SPIKE DUPLICATES: A second aliquot of the same sample used for matrix spike spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.11. METHOD BLANK: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank must be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process. For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern shall not be higher than the method detection limit

4.12. METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of seven analyses of a matrix spike containing the analyte of interest at a concentration one to five times the estimated MDL.

4.13. ORGANIC-FREE REAGENT WATER: All references to water in the method refer to water in which interference is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free de-ionized water.

4.14. PRECISION: The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate analyses. These samples should contain concentrations of analyte above the MDL, and involve the use of matrix spikes or laboratory fortified blanks. The estimates of precision are based on the relative percent difference (RPD).

$$RPD = 100 [2 (X1 - X2) / (X1 + X2)]$$

where X1 and X2 are the two measurements

4.15. INITIAL CALIBRATION VERIFICATION (ICV): A standard solution from a source, other than normal calibration standards, that is certified and traceable. These standards are used to check the accuracy of a calibration curve immediately after the calibration standards are run.

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4.16. CONTINOUS CALIBRATION VERIFICATION (CCV): A standard solution from a source that is certified and traceable. These standards are used to check the accuracy of a calibration curve.

4.17. SPIKE SOLUTION (SS): A solution of method analytes of known concentrations that is used to fortify an aliquot of laboratory reagent water or sample matrix.

4.18. STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards, which cover the working range of the instrument. Standards should be prepared at the frequency specified in section six (6) of this SOP. The calibration standards should be prepared using the same type of solvent as the final sample preparation solvent.

4.19. SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Surrogates are used to monitor the preparation and are added to each field and QC sample prior to extraction.

5. APPARATUS AND EQUIPMENT

5.1 Apparatus.

Agilent 7000C GC/MS/ triple quadrupole system or Agilent 7010 GC/MS/MS or equivalent. Must be temperature programmable with an injector port designed for cold splitless injection. A Multi-Mode Inlet (MMI) may be used if available. The GC, GC Automatic Sampler and MSD operating parameters are illustrated in Tables 2, 3 and 4. The analytical column is an HP-5MS UI or equivalent, fused silica capillary, 20 m x 0.25 mm x 0.25 um or similar column with Ultimate Union placed after the initial 5 m of the column (5m-15m mid-column backflash configuration).

5.2 Data system

5.2.1 A computer system is interfaced to the GC/MS/MS that allows the continuous acquisition and storage on machine-readable media of all chromatographic measurements obtained throughout the duration of the chromatographic run sequence program.

5.2.2 This system currently uses the Masshunter software from Agilent Technologies Inc. For reporting data, the system currently uses DEP LIMS.

5.3 Gases

5.3.1 Helium, UPC Grade or higher, is used as the carrier and collision cell gas. The helium is passed through an oxygen and a hydrocarbon filters before it enters the GC.

5.3.2 Nitrogen, UPC Grade or higher, is used as a collision cell gas. The N_2 is passed through a hydrocarbon filter before entering the GC.

6. REAGENTS AND CHEMICALS

6.1. Solvents

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6.1.1. Methylene Chloride, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.

6.1.2. Isooctane, Fisher Scientific, Pesticide, HPLC or OPTIMA grade.

6.1.3. Acetone, Fisher Scientific, Pesticides, HPLC or Optima grade.

6.2. Standards

6.2.1. For detailed standard preparation see APPENDICES 1 and 2

6.3. Stock and Intermediate Standards

6.3.1. Custom made stock standards and/or neat standards for individual analytes available) are purchased from commercial suppliers. The concentrations of (two different sources or two different lot numbers if only one vendor is currently purchased) custom made standards are listed in the appendix 1: "Preparation of pesticides standards".

6.3.2. Intermediate standard solutions are mixtures of individual standards used to prepare working standards. They are prepared in our lab from stock standards by mixing / diluting with isooctane or acetone. They can also be purchased from a certified manufacturer (ISO 9000 or EPA certified). The concentrations of the components in the intermediate standard are typically several mg/L. Intermediate standards are replaced once per year. New standard is checked vs. a second source (QC Standard), after diluting it to one of the working standard levels. The criterion of acceptance is +/- 10% difference. All standard preparations and verifications have to be recorded in the Standard Preparation Tracker located in DEP LIMS. A list containing all standards with their serial numbers used in the analysis must be part of analysis documentation folder. Currently standard serial numbers are entered in the analysis run sequence.

6.4. Working Standard Solutions (Calibration standards)

6.4.1. Working standard solutions are a series of diluted individual or mixture standards in isooctane:acetone 4:1 v/v, pure isooctane is used for chlorinated pesticides.and PCBs. They are used for calibration and are prepared by diluting intermediate standard solutions. The internal standard mixtures listed below are added to every working standard at 100 μg/L.

Internal Standard Mixture for NP analytes:

Tributyl Phosphate-d27
Atrazine-d5
Hexazinone-d6
Parathion Ethyl–d10

Internal Standard Mixture for CL analytes and PCBs:

Alpha-BHC-d6
2,5-Dichlorobiphenyl-2',3',4',5',6'-d5 (DCB-d5)
2,3,5,6-Tetrachlorobiphenyl-2',3',4',5',6'-d5 (TCB-d5)
2,3,3',4,4'5-Hexachlorobiphenyl-2',6,6'-d3 (HCB-d3)
DDT-p,p'-d8
Trifluralin-d14

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Dicofol-d-8
Octachloronaphthalene

6.4.2. The concentrations for each analyte in the working (calibration) standards are listed in Table 5A for Nitrogen Phosphorus analytes, in Table 5B for chlorinated pesticides, in Table 5C for PCB Aroclors, and in table 5D for chlorinated pesticides/ PCB congeners for tissue analysis. The second source/CCV standard is prepared at midpoint level.

6.5. Spiking Solution

6.5.1. These solutions are used when fortifying sample matrix spikes or lab fortified blanks at extraction. These fortified samples are used to verify the accuracy and precision of the sample preparation and analysis.

6.5.2. Spike solutions are prepared by diluting stock or intermediate standards with acetone. Concentrations of the parameters in these solutions are listed in tables 5A,5B, 5C and 5D.

6.5.3. Freshly prepared spike solutions are checked vs. valid working standards. The acceptance criterion is ± 20% difference.

6.6. Initial Calibration Verification (ICV) A standard solution from a source, other than normal calibration standards, that is certified and traceable. These standards are used to check the accuracy of a calibration curve immediately after the calibration standards are run. The acceptance criterion is ± 30%.

6.7. Continuous Calibration Verification (CCV). A mid-level calibration standard solution from a source that is certified and traceable. These standards are used to check the accuracy of a calibration curve on daily bases.

6.7.1 The acceptance criterion is ± 20% difference.

6.7.2 The Analyst must insure that the calibration standards are checked with the corresponding CCV with every initial calibration and then in 12 hrs intervals thereafter.

6.8 Analyte protectants.
The use of analyte protectants was proposed by Anastassiades et al. (ref 15-3 and 15-4) and it has become an established practice for pesticides analysis in food products analysis, where triple quad GC/MS/MS technology has found the widest use. Agilent 7000C GC/MS/MS instrument is very sensitive to matrix induced response enhancements which makes exact quantitation problematic. Analyte protectants are generally very polar organic compounds injected at very high concentrations along with every standard and sample in the analytical run sequence. Due to their polarity, they are thought to deactivate all the active sites in the system, and, due to their very high concentration, to render all the other matrices in the samples basically insignificant. In effect all the samples and standards injected into the GC/MS/MS system have effectively the same matrix – the analyte protectants – and therefore matrix induced response differences are greatly reduced. This method uses a mixture of three specific analyte protectant compounds: Ethoxyglycerin, Gulonolactone and Sorbitol at 25000 ppm, 2500 ppm and 5000 ppm respectively. Due to solubility considerations, the working solution is prepared in MeOH containing 5% of DI water. It is injected along with every standard and sample using a "sandwich injection" technigue. 0.4 uL of the above analyte protectants mixture is

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injected, which corresponds to 10 ug, 1 ug and 2 ug of the corresponding analyte protectants on column.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1. Samples must be collected in glass containers with Teflon-lined screw caps.

7.2. All samples must be refrigerated at -4 degrees C or less from time of collection until extraction.

7.3. All samples must be extracted within 7 days of collection (waters) or 14 days of collection (soils, wastes) or 365 days (tissue samples) and completely analyzed within 40 days of extraction. . If the water samples are to be analyzed for Aldrin and residual Chlorine is present, then add 80 mg of Sodium Thiosulfate per 1 L of sample and mix well.

8. SAMPLE PREPARATION PROCEDURE

8.1. See Preparation SOP GC-002: Extraction of pesticides and polychlorinated biphenyls (PCBs) from Water Wastes, soil/sediments PUFs and filters for subsequent analysis by GC-ECD/NPD or GC/MS/MS. (ref 15.2). Also refer to Appendix 6: “Preparations Flowcharts”

8.2. For test W-PSNP-TQ 1L water samples are extracted with Methylene Chloride (3×60 mL) to a final volume of 0.25 mL. 0.2 mL is submitted for analysis to account for the addition of 50 uL of 500 ug/L NPTQ internal standard solution.

8.3. .

8.4. For Dieldrin by W-DIELDRIN test 500 mL water samples are extracted using C-18 SPE cartridges at pH=2, eluted with methylene chloride and brought down to 0.25 mL in Isooctane. 25 uL of 1000 ug/L PSCL internal standard is added before the final blowdown.

8.5. For soil samples (S-PSNP-TQ, S-PSCL-TQ and S-PCB-TQ) 30 g of sample is extracted with 1:1 methylene chloride/acetone (sonication), solvent exchanged to isooctane and then concentrated to 2 mL of final volume.

8.6. Tissue samples (test ID T-PCBCL-TQ, T-PCB-TQ) are extracted according to SOP GC-004-1 (ref 15-16); 5 g samples are extracted with methylene chloride using Dionex ASE350 machine. The extracts are solvent exchanged to isooctane and blown down to 2 mL.

8.7. Both soil and tissue extracts are further cleaned up by using GPC (NP pesticides), GPC/Florisil (chlorinated pesticides and PCBs) or H2SO4/TBA (some chlorinated pesticides and PCBs) methods. 1mL sample is typically vialed for GPC clean-up; 0.8 mL is injected and 0.7 ml is submitted to allow for the ISTD addition (100 uL of 800 ppb solution). If sulfuric acid /TBA cleanup is performed 1mL of sample is used and blown down to 900 uL to allow for the Internal standard addition (100 uL of 1000 ppb solution.)

8.8. Extreme care has to be exercised by all the laboratory staff involved in preparation and analysis to limit background contamination due to ultralow detection limits achievable with the Agilent 7000C GC/MS/MS system. DI water should be used to perform both method blanks and Laboratory Fortified Blanks due to low level pesticide contamination usually found in both tap water and well water.

9. GENERAL DESCRIPTION OF GC/MS/MS ANALYSIS

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9.1. GC/MS/MS Maintenance and Tuning

9.1.1 DFTPP tune recommended by EPA 8270D is not applicable for Agilent 7000C 7010 GC/MS/MS. Instead, as recommended by 8270D paragraph 11.3.1, this SOP modifies the method to follow manufacturer's tuning instructions. GC/MS/MS tuning includes periodically performed autotune as well as a daily tune check.

9.1.2 Initial checking and maintenance of the instrument consists mainly of the following steps:

9.1.2.1 Check the vacuum operation and periodically run an air/water leak test. Oxygen, nitrogen and water have to be found at below 5% of mass 69 level. Air/water leak test must be run each time the vacuum system is vented. It may take several hours (even overnight) of pumping down to bring the air/water content below 5%!

CAUTION: In order to properly perform the air/water leak test nitrogen gas flow to the collision cell has to be turned manually off at the source! After the test, nitrogen gas has to be turned back on!

9.1.2.2 Perform the triple quadrupole GC/MS system verification (tune check) before each run sequence. Print the tune check report and include with the documentation. The tune check requirements are listed in appendix 3. Periodically perform the EI high sensitivity autotune of the GC/MS/MS triple quadrupole system and save the current settings in the autotune file. The autotune has to be perform, however, every time the tune check fails. The report is printed automatically and it should be placed in the autotune reports log. If the autotune criteria are not met repeat the autotune. If still failing, run the autotune from the default values. If that fails the ion source may have to be cleaned. **It is not recommended to attempt manual tune of the instrument without the assistance of the Agilent Technologies' triple quad trained specialist!**

9.1.2.3 Replace the injector liner (Agilent's 2 mm dimpled liner part no: 5190-2296 is recommended for cold splitless injection), cut 1-3 inch of the column after running contaminated samples or encountering unusually heavy matrix. Occasional trimming of the column is still necessary even if backflush technology is used.

9.1.2.4 Run an Instrument Blank and look for instrument contamination.

9.1.2.5 In case the instrument is contaminated raise the furnace temperature to 260 ^{o}C and leave it overnight.

9.1.2.6 To perform maintenance of the MMI inlet replace the liner and septum and clean the inside of the inlet body with cotton swabs soaked with methanol and methylene chloride. **Do not use a harsh brush to clean the inside of the inlet body!** To complete the MMI inlet cleaning perform an inlet bake out procedure. Set the inlet mode to split (split ratio 200:1) and let the gas flow for a couple of minutes. Then raise the inlet temperature to 330 ^{o}C and the oven temperature to 300 ^{o}C. Bake for 1-2 hrs. It is beneficial and recommended to bake the ion source at 350 ^{o}C at the same time.

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9.1.2.7 The autosampler syringe has to be frequently and thoroughly cleaned to avoid injection repeatability problems. A dirty plunger will cause reproducibility problems, bad injections occurring randomly, and poor peak shapes and calibration problems. Replacing the syringe on regular, frequent basis is highly recommended.

9.1.2.8. Re-check for instrument contamination and if needed repeat the procedure until the instrument is contamination free.

9.2 GC/MS/MS System Initial Calibration

9.2.1. Analyze the calibration standards at the following levels listed in Tables 5A, 5B and 5C, 5D. At each level, the internal standards should be present at 100 µg/L. The linearity of the calibration curve is defined by an RSD that is less than or equal to 20% of the Response Factors of the calibration curve, or by a correlation coefficient not smaller than 0.995. If a higher order curve is to be used the correlation coefficient has to be at least 0.995. When new calibration is inspected linear fit is usually tried first, followed by average response factor (%RSD which is equivalent to weighted linear forced through origin), then followed by quadratic fit and finally higher order curves. Do not use the "include" origin option in the Masshunter software. "Ignore" origin is preferable to "force" through origin in most cases. Forcing the curve through origin is acceptable whenever ignoring origin produces nonsensical results for small peaks close to MDL (like negative values). When calibration curve fit is selected in the Masshunter software the % calibration drift has to be monitored in order to have all the calibration levels within 70-130% of the expected value. Special care has to be taken to carefully fit the curves at the lower end of the calibration range where the vast majority of problems occur. Weighting of the calibration curve is frequently necessary to accomplish that goal. It is permissible to remove individual analyte calibration levels from either the lowest and/or highest levels of the curve (the PQL may have to be adjusted). Removal of interior levels is forbidden. An entire single standard calibration level may be removed from the interior of the curve whne the standard was not correctly injected or a wrong standard was injected. If more than 10% of the total number of analytes fail the calibration fit criteria or more than 20% of analytes fail the % calibration drift criteria, then the instrument system must be corrected. Some possible problems include standard mixture degradation, injection port inlet contamination, analytical column contamination, and active sites in the column or chromatographic system.

9.2.2. Each time the column length is trimmed due to contamination or a new column is installed the retention times for each compound have to be re-determined . The MRM mode time segments (acquisition windows) or retention times (for the dMRM methods) have to be then adjusted accordingly. A mid-level standard should be then run to confirm that all the peaks are fully within the acquisition windows. Both the analysis end of the method (Masshunter) as well as the data-gathering end of the method (Acquisition) must be adjusted. Alternatively, RT locking procedure can be used to keep the retention times uchanged after the column is trimmed. Approximate retention times, the primary quantitation transitions and confirmatory, secondary transitions (if available) are given along with MRM acquisition time segments start/stop times in Table 4A , 4B, 4C, 4D, and 4E. The primary and secondary ions should all be present and the relative intensities should agree within ±30% (absolute) of the reference mass spectrum after background subtraction is performed.

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9.2.3 Initial calibration curve is always immediately checked with the second source initial calibration verification standard (ICV). The acceptance criterion is ±30%. If the Initial Calibration is not run with the batch, the CCV acceptance criterium is +/- 20% (see 9.3.2)

9.3 Daily GC/MS Performance and Calibration Check

The initial calibration curve and instrument performance must be verified on each day of analysis by the measurement of one or more check standards.

9.3.1 Degradation/tailing factor check
A modified GC/MS tuning standard is used to perform this task. The standard contains 5 mg/L each of DDT-p,p'and Pentachlorophenol. Benzidine, which is also recommended by method 8270D, is usually not detectable in the presence of analyte protectants. Since the absence of benzidine peak in the chromatograms has no bearing on the chromatographic behavior of the target analytes and surrogates, only pentachlorophenol is used for the tailing factor determination. The degradation check/tailing factor standard is run at the beginning of the analytical run sequence to verify injection port inertness and GC column performance. A full scan version of the acquisition method is used for this purpose. Degradation of DDT to DDD and DDE should not exceed 20%.
The percent breakdown calculation is performed using the following formula (EPA method 8081)

%Dec. DDT = Sum Peak Area (DDE + DDD) / Sum Peak Area (DDE + DDD + DDT) × 100%

The following are the Relative Retention Times for DDD-p,p' and DDE-p,p' (relative to DDT-p,p'):
DDE-p,p' RRT = 0.885
DDD-p,p' RRT = 0.949

Usually it is necessary to perform spectral deconvolution of the chromatograms to remove the analyte protectants "hump" and obtain correct integration values and clean spectra for target analytes.

The tailing factor for pentachlorophenol should not be higher than 2 according to the following equation:

Tailing Factor = BC / AB

Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and B is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. If DDT-p,p' degradation and or tailing factors are excessive the injection port maintenance has to be performed until proper chromatographic performance is restored.

9.3.2 Analyze midpoint level standards as continuing calibration check (CCV) standards. These calibration check standards must be analyzed at the start of each run and at 12-hour intervals thereafter. The acceptance criteria for all components are 80-120% recovery. If multiple CCV failures are observed corrective action must be taken prior to the analysis of samples. When compounds fail, they may still be reported as non-detects (with a "J" qualifier) if it can be demonstrated that there was adequate sensitivity to detect the

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compounds at the applicable quantitation limit. For situations when the failed compound is present, the concentrations in the affected samples must be reported as estimated.

9.3.3 Calibration verification standard must also meet the following criteria:

9.3.3.1 Internal standard responses: the peak area for each of the internal standards may not change beyond the factor of two (-50% to +100%) from that of the average internal standard response of all the levels in the most recent initial calibration.

9.3.3.2 Internal standards retention times- the retention times of the internal standards in the calibration verification standard must not drift by more than 30seconds from that of the mid-point standard level of the most recent initial calibration.

9.3.3.3 If any of the requirements mentioned in 9.3.3 are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites in the column or chromatographic system, and a contaminated MS source.

9.4 GC/MS/MS Sample Analysis.

9.4.1 Quantitative analysis of all analytes is accomplished by the internal standard calibration method. All target component positives found have to be quantified using at least a five-point calibration curve (for linear fit), at least six points for quadratic and at least seven points for higher order curves. Each sample extract MUST contain 100 µg/L of each internal standard. Any extract that is determined, in initial analysis, to contain high concentrations of any of the target analytes should be diluted as deemed necessary. **The concentration of internal standard must remain at 100 µg/L when diluting samples by adding additional internal standard to the extract.**

9.4.2 Analysis Run Sequence.

The analyst will set up an analysis run sequence by placing the GC vials containing the sample extracts and standards on the autosampler tray in the following order or similar:

- isooctane (to clean the system)
- degradation/performance check
- Instrument Blank (containing internal standards at 100 ug/L)
- pesticides calibration set (when initial calibration is run, levels 1-8)
- ICV initial calibration verification check (when initial calibration is run)
- CCV continuing calibration check
- extraction blank
- diatomaceous earth blank (tissues only)
- laboratory fortified blank (LFB)
- laboratory fortified blank duplicate
- sample matrix spike,
- sample matrix spike duplicate
- samples (for up to 12 hrs)
- CCV continuing calibration check

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- samples (for up to 12 hours)

9.4.3 Print a hard copy of the run sequence and place it in the final data folder.

9.5 Analysis of PCB Aroclors using GC/MS/MS

9.5.1 The acquisition method for PCB Aroclors (AR_MRM_yymmdd) contains, in one single acquisition segment, 21 individual PCB transitions along with transitions for internal standards (three deuterated PCB congeners are used). The list of PCB transitions include at least one transition for each level of chlorination plus a number of other transitions prominent in specific Aroclors. The use of single acquisition window ensures that the entire PCB pattern can be recreated by summing up all the different transitions. All the individual transitions used in the acquisition method are listed in Table 4C-1. The individual PCB transitions listed in the acquisition method each reconstruct parts of the Aroclors pattern, over certain RT spans; they will each show as clusters of PCB peaks at different RTs in different parts of the chromatogram. Those peaks would, usually, be common for two or more individual Aroclors. Therefore correlation between the acquisition transitions and the analytical Aroclor peaks is not straightforward. The typical Aroclor analytical peaks with their quantifier and qualifier transitions are listed in Table 4C-2. Analyst will select 5 analytical peaks for each Aroclor that cover the entire RT range and include major transitions for that particular PCB aroclor.

9.5.2 Identification of PCB Aroclor pattern is accomplished by visual comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made by the analyst whether that standard is truly representative of the PCBs in the sample. Individual Aroclor standards are run for PCBs 1221, 1232, 1242, 1248, 1254 along with PCB 1016/1260 mixture (also referred to as PCB-1060). The visual comparison is accomplished in Qualitative Software by extracting the relevant chromatograms in the EIC-MRM mode. Once the identification is made the relevant chromatograms are printed out and included with the documentation. Refer to appendix 6 for PCB Aroclor patterns and analytical peaks.

9.5.3 Although this SOP is based on EPA method 8270D the quantitation algorithm of the PCBs Aroclors analysis essentially follows the EPA method 8082A (Polychlorinated Biphenyls (PCBs) by Gas Chromatography) (ref 15.5). Method 8270D (ref 15.1)states in paragraph 11.7.5 that quantation of mulicomponent compounds such as Aroclors is beyond its scope, and refers to GC/ECD methods (i.e.; 8082).

9.5.4 The analytical run sequence for the PCB Aroclors analysis includes a full six point calibration for PCB 1016/1260 mix along with single standards for the five remaining individual Aroclors, for pattern identification purposes. during the days after the initial calibration and PCB patterns are run, it is sufficient to run only PCB-1060 CCV, provided that no retention time changes occurred (no column cutting!). If the CCV fails or other factors occur (such as ion source cleaning, column cutting or replacement) the entire initial calibration has to be run again..If no PCBs are identified in the sample, non- detects are reported. Positive hits for PCB 1016 and 1260 can also be reported, provided their concentrations do not exceed the calibration range. If any of the remaining Aroclor is identified, the samples must be rerun along with a full calibration for that particular Aroclor. Surrogate Decachlorobiphenyl is included in the PCB

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1016/1260 mix and therefore it may be analyzed in the original PCB analytical run sequence.

9.5.5 Once the Aroclor pattern has been identified the quantitation of Aroclors is accomplished by using 5-major peaks characteristic for each individual Aroclor (see table 4C-2). For the best results those peaks should be evenly spread over the entire Aroclor pattern. A separate calibration curve is build for each of the individual analytical peaks. The concentration for the total Aroclor is then assigned to each analytical peak. The amount of the Aroclor is calculated using the individual calibration factors for each of the 5 analytical peaks and the calibration model established (linear or non-linear) from the multi-point calibration. Different calibration models may be used for each selected peak. The concentrations obtained for those five analytical peaks are then, finally, averaged to determine the concentration of that Aroclor.

9.5.6 Weathering of PCBs in the environment and changes resulting from waste treatment processes may significantly alter the PCB patterns. Averaging of five, carefully chosen, analytical peaks provides for some ability to overcome weathering effects and still obtain acceptable quantitation results. To accomplish that, it is essential not to attempt to" reverse match" the analytical peaks used for calibration to those identified in the degraded sample pattern. Instead, the individual concentrations calculated for the analytical peaks are summed up and still divided by five, even if some peaks are missing in the sample.

9.5.7 In some cases it may be advisable to use the total area approach to calculate the concentration in a weathered Aroclor sample. Great care must be exercised, however, to ensure that no interfering compounds elute in the same portion of the chromatogram.

9.5.8 Additional PCB aroclor standard called PCB-1268 maybe be run in some cases, especially when there is a reasonable suspicion that PCB congeners higher than those commonly found in PCB-1260 are present in the sample. PCB-1268 is not currently a target analyte in S-PCB-TQ test. However, the presence of PCB-1268 pattern indicates the presence of Decachlorobiphenyl (PCB-209, a component of PCB-1268 pattern) in the sample. Since Decachlorobiphenyl is used as a surrogate, such samples will typically have that surrogate failing high. It is therefore not necessary to report Decachlorobiphenyl surrogate in such samples.

9.5.9 In case when two overlapping PCB aroclors are present in the sample, it is permissible to select different peaks for quantitation. This includes situations when an estimate of the Total Aroclor concentration is requested by the client.

9.6 Data Processing using the Masshunter software.

9.6.1 Using the Qual software examine the degradation/performance check sample. Calculate DDT decomposition and the tailing factor for pentachlorophenol.

9.6.2 Examine the quantitation reports soon after the samples have been analyzed. Check all of the calibration check standards analyzed during the run sequence and insure that they met the minimum criteria given above.

9.6.3 The concentration reported for an identified hit in the sample extract, expressed in ug/L, is quantitated using the initial calibration curve. However, the analyst must ensure that all identification criteria are fulfilled and the peak area integration was correctly done. If not, the integration has to be re-done by

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choosing a new set of integration parameters or by manual integration (see SOP CM-018.1 for lab manual integration, ref 15.12).

9.6.4 If the response for any of the compounds exceeds the calibration curve, the extract must be diluted so that the response will be within the limits of the curve, and then reanalyzed. Make sure when performing dilutions to use isooctane spiked with the appropriate levels of internal standard so that their response will be the same in the dilution as it was in the original extract.

9.6.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after data acquisition. If the retention time for any internal standard changes by more than 0.05 minutes from the last calibration, then the chromatographic system must be evaluated for either a) chromatographic matrix induced shift or inspected for malfunctions (such as leaks) and corrections must be made. The m/z abundances for all of the internal standards must be within a factor of two (50% to 200%) from the abundance in the daily calibration standard check. Corrective action is indicated if the m/z abundance is outside of these limits. If the holding time for a sample has expired and the internal standard areas are out of the acceptance range, then the final report must be commented and any positives detected must be qualified with a "J" to indicate that the result is an estimate.

9.6.6 Analysis of surrogates.

9.6.6.1 The analyst should monitor the performance of the extraction, cleanup, analytical system, and effectiveness of the method by spiking each sample, QC samples and Method Blanks with the NP-TQ surrogate spike solution currently containing Simazine-d10 and /Terbufos-d10 at 100 ug/L, or PSCL surrogate spike solution currently containing Decachlorobiphenyl and Tetrachloro-m-xylene at 200 ug/L. Both chlorinated surrogates are used for tests W-DIELDRIN, S-PSCL-TQ, S-PCB-TQ and T-PCBCL-TQ. . The surrogate compounds are expected to be found at 20 µg/L in all the sample extracts, Blanks, LFBs, and Matrix Spikes. Except for the W-DIELDRIN test where the expected extract concentrations are 40 ug/L for both chlorinated surrogates.

9.6.6.2 To determine the acceptance accuracy limits for a surrogate the following procedure should be used (ref 15.5): (1) for each sample analyzed, calculate the percent recovery of each surrogate in the sample, (2) once a minimum of thirty samples of the same matrix has been analyzed, calculate the average percent recovery (p), and standard deviation of the percent recoveries (s), for each of the surrogates, (3) for a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard as follows:

Upper Control Limit (UCL) = p + ts
Lower Control Limit (LCL) = p – ts
Where “t” stands for Student’s coefficient for n-1 degrees of freedom (n = number of measurements).

The control limits are supposed to be checked once per year if enough measurements have been conducted. For new surrogates, the initial acceptance limits of about 50-150 % will be used until enough statistical data is acquired to perform the necessary calculations.

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9.6.6.3 If a surrogate recovery fails low, the sample has to be re-extracted and re-analyzed, even if the holding time time for extraction is already exceeded. If the recovery is biased high, the re-extraction is not required and the reported hits have to be qualified as estimated (J). An automatic comment will be generated by LIMS.,..

9.6.7 Analysis of matrix spikes and LFBs

Check the Matrix Spike and Lab Fortified Blank recoveries. They must be within the current acceptance ranges. A comment must be added to the final report explaining any deviation from the routine recoveries whenever the spikes or surrogates are out of range. Matrix spikes and LFBs recoveries should be calculated based on available in house data once enough data points are collected. The limits are established as in 9.6.6.2. LFBs and Matrix spikes recovery limits are calculated independently; see Table 6 for details.

9.6.8 Blank contamination

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(s) rerun/reanalyzed.
In the event a positive identification is found in both the sample(s) and the extraction blank then the sample set has to be re-extracted and reanalyzed. If samples passed the holding time, the results will be reported with a "V" qualifier up to ten times the amount found in the blank.

9.6.9 Continuing Calibration

9.6.9.1 After initial calibration, the GC/MS/MS response is checked immediately by running an Initial Calibration Verification standard (ICV) and then, on a continuing basis (every 12 hours), by using a continuing calibration check (CCV), middle range pesticides standard. Criterion of acceptance for continuing calibration check is +/-20 % of initial calibration. If a CCV fails, all the samples run after this standard, have to be re-run for all positive hits found at concentrations higher than PQL level. If the samples have exceeded the analysis holding time then all hits must be flagged as estimated.

9.6.9.2 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 (see 15.6 for more details).

9.6.10. Quantitation of positives.

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Positives are quantified based on their peak area. The concentration reported for an identified hit in the sample extract, expressed in ug/L, is based on calibration curve of the initial calibration. The Masshunter software used to process data will do the interpolation for the sample extract. However, the analyst must ensure that all identification criteria are fulfilled and the peak area integration was correctly done. If not, the integration has to be corrected by choosing a new set of integration parameters or by manual integration (for manual integration procedure see 15.12). Only extract concentrations are calculated by the processing software. The final analyte concentrations in sample are calculated in the QC Manager during the data upload process software. This is done as follows:

- C_{sample} (ug/kg) = (C_x) × ($V_{extract}$) × (DF)/(W_{sample}) for sediment and waste and tissue

- C_{sample} (ng/L) = (Cx) × ($V_{extract}$) × (DF)/(V_{sample}) for water samples

where:

- C_x - The concentration, in ug/L, of the analyte in the sample extract determined by the processing software.

- $V_{extract}$ -The volume of the extract, in mLs (usually 0.25 or 10 or 2 mLs) recorded in the preparation report.

- DF - The dilution of the sample extract recorded in the dilution report.

- W_{sample} - For sediment it is the dry weight of the sample that was extracted. For waste and tissue it is the weight of the sample taken for extraction. The weights are expressed in grams and are recorded in the preparation report.

- V_{sample} -This is the volume of the water sample taken in extraction, expressed in mLs (usually 1000 mL).

10 REPORTING AND DOCUMENTATION

10.1 When analysis is complete, generate a .txt file in the Masshunter software for all the reported samples, QC samples and CCVs. The QC Manager is then used to download the final sample results into the Laboratory Information Management System (LIMS). If a sample has been diluted then make sure that the information was entered properly into the QC Manager. The following convention should be used in QC calculator:

NP_CCV or CL_CCV or PCB_CCV for CCV
SURNP_CCV or SURSNP_CCV or SURCL_CCV or SURRPCB for surrogate in CCV
SURNP_1234567 or SURSNP_1234567 or SURCL_1234567 or SURDLD_1234567 or SURRCLT_1234567 or SURPCB_1234567 for surrogate in sample

10.2 The QC manager will convert the data from ug/L to ng/L (LIMS reporting units, water samples only; not applicable for soils and tissues) and also it will add MDLs for all analytes not included in the text file (nondetects). The converter will also average the PCB aroclors result and report the average as the corresponding aroclor.

10.3 Add the appropriate qualifiers and comments to the sample data in the QC Manager after performing a complete review of the sample data and QC data. Follow DEP SOP OG-003-

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Data Review/Authorization Checklist (ref 15-6) for details of data review and reporting, See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data (ref 15-7) for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option. Definitions of the available qualifying codes are listed in DEP SOP LB-027

10.4 All quantitation reports for samples and QC should be placed in a results folder labeled with the job number, the sample numbers, and the type of analysis.

10.5 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of dilutions page if any. Also include a print out of sample positives from the data review (a scrollable report) and file it in the data folder.

10.6 Submit the result folder to the GC pesticides section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the GC-pesticides filing cabinets.

11 QUALITY CONTROL

11.1 See DEP SOP GC-001, Quality Assurance/Quality Control in the GC Pesticides Laboratory (ref 15.8) for detailed information on quality control, definitions and interferences. See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data (ref 15.7) for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

11.2 All data generated by a chemistry analyst are subjected to supervisory review and authorization. The supervisor is assessing the validity of data generated by assuring that all QA/QC criteria are met by checking the following review/authorization checklist:

- Check sample preparation report
  - procedure
  - surrogate and spiking solutions
  - preparation holding time
- Check project log-in folder for special requests
- Check initial calibration for linearity and fit
- Check continuing calibration check standards
- Check surrogate recoveries
- Check accuracy and precision for LFB and Matrix Spikes
- Check internal standard recoveries
- Check retention time drift
- Check for blanks contamination
- Check for positives:
  - Proper integration of the peaks (baseline)
  - Retention time confirmation
  - Amount confirmation
  - If response is within the calibration range
  - Calculations
  - Qualifiers
  - Proper identification of Aroclor patterns
- Check information in the MassHunter Report Header:

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- SOP #
- Instrument ID
- Analyst name

- Evaluate the data against any field information
- Check field preservation record
- Check LIMS report:
  - Preparation and analysis dates
  - MDLs
  - Amounts reported for positives
  - Qualifiers
  - Comments

12 DATA ARCHIVAL

12.1 All raw data are retained in electronic or hard copy format. All paper formats are maintained either in the laboratory office or in a State warehouse for at least ten years. Electronic chromatographic raw data are archived by analysis file ID and instrument ID on dual CDs by the Laboratory Support Section.

12.2 Move the valid data files (tune, ICALS, CCVs, QC and sample data files) soon after collection from the hard disk of the instrument computers to the network drive \\TLHLAB3\GC\BACKUP_GC_TQ-1 (or TQ-2, or TQ-3). Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or whenever they are no longer needed.

12.3 Copy the processed data files Quantitation reports (Masshunter .txt files) into \\TLHLAB3\GC\UPLOAD_GC_TQ-1 (or TQ-2, or TQ-3) to convert in QC Manager for reporting in LIMS. These files may be deleted after all results are authorized.

13. DETERMINATION OF METHOD DETECTION LIMITS

13.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register (ref 15.3). Also refer to Reference 15.9 and 15.10**.**

13.2 Seven replicate samples are analyzed near the MDL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

13.3 The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically to establish or update the MDLs and PQLs for each analyte and matrix.

14. SAFETY/HAZARDOUS WASTE MANAGEMENT

See SOP OG-001, Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories) (ref 15.11) for specific details on safety and hazardous waste management.

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15. REFERENCES

15.1 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8270D, Semi-volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS).

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15.2 GC SOP GC-002: Extraction of pesticides and polychlorinated biphenyls (PCBs) from Water Wastes, soil/sediments PUFs and filters for subsequent analysis by GC-ECD/NPD or GC/MS/MS.

15.3 Anastassiades, M., Mastovska, K., Lehotay, s.J., "Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides" Journal of Chromatography A, 1015 (2003) 163-184.

15.4 Mastovska, K., Lehotay, S.J., Anastassiades, M., "Combination of analyte protectants to overcome matrix effects in routine GC analysis of pesticides residues in food matrices" anal. Chem. **2005**, 77, 8129-8137.

15.5 EPA 8000C Determinative Chromatographic Separation; Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW 846; 3rd Edition, Update 4, January 3, 2008.

15.6 DEP SOP OG-003. Data Review/Authorization Checklist

15.7 DEP SOP LB-027. Standard Operating Procedure for Reporting Qualified Data.

15.8 DEP SOP GC-001. Quality Assurance/Quality Control in the GC Pesticides Laboratory

15.9 Florida Department of Environmental Protection, Standard Operating Procedure LB-007 *Procedure and Policy for Method and Instrument Validation.*

15.10 Florida Department of Environmental Protection, Standard Operating Procedure LB-031 *Limit of Detection Verification.*

15.11 DEP SOP OG-001. Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories).

15.12 DEP SOP CM-018-1 Laboratory Policy Regarding Manual Chromatographic Peak Integration.

15.13 Code of Federal Regulations, Title 40, Part 136, Appendix B.

15.14 Wylie, P., Meng, Chin-Kai, "A Method for the Trace Analysis of 175 Pesticides Using Agilent Triple Quadrupole GC/MS/MS" Agilent Technologies Application Note.

15.15 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8082A, Polychlorinated Biphenyls (PCBs) By Gas Chromatography

15.16 DEP SOP GC-004 Extraction of Organophosphorus, organonitrogen, organohalide pesticides and PCBs from Fish Tissue for subsequent analysis by GC-NPD/ECD

15,17 DEP SOP GC-036-1. Analysis of Chlorinated Pesticides in water samples using Solid Phase Extraction and GC/MS-SIM.

16. TABLES

TABLE 1A-Water: Internal standard associations, MDLs, PQLs and approximate RTs for Nitrogen Phosphorus pesticides included in LIMS test W-PSNP-TQ. **LIMS reporting units are ng/L (ppts)**

Analyte	Approximate Retention	Associated internal standard	MDL (ug/L)	MDL (ng/L)	PQL (ug/L)	PQL (ng/L)

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	Time (min)					
			extract	sample	extract	sample
Simazine-d10 surrogate	6.13	Atrazine-d5				
Terbufos-d10 surrogate	6.00	Tributyl Phosphate-d27				
EPTC	4.30	Atrazine-d5	5.0	1.30	20	5.0
Butylate	4.58	Atrazine-d5	1.6	0.40	6.4	1.6
Mevinphos	4.64	Tributyl Phosphate-d27	2.0	0.50	8.0	2.0
Molinate	5.09	Atrazine-d5	1.2	0.30	4.8	1.2
Demeton*	5.44 –"O" 6.09 - "S"	Tributyl Phosphate-d27	8.0	2.0	32	8.0
Ethoprop	5.57	Tributyl Phosphate-d27	0.40	0.10	1.6	0.40
Atrazine Desethyl	5.78	Atrazine-d5	6.0	1.5	24	6.0
Phorate	5.90	Tributyl Phosphate-d27	1.0	-.25	4.0	1.0
Simazine	6.17	Atrazine-d5	2.0	0.50	8.0	2.0
Prometon	6.18	Atrazine-d5	3.6	0.90	14	3.6
Atrazine	6.21	Atrazine-d5	1.0	0.25	4.0	1.0
Terbuthylazine	6.37	Atrazine-d5	1.7	0.43	6.8	1.7
Terbufos	6.36	Tributyl Phosphate-d27	0.40	0.10	1.6	0.40
Fonofos	6.41	Tributyl Phosphate-d27	0.80	0.20	3.2	0.80
Diazinon	6.49	Atrazine-d5	0.50	0.13	2.0	0.50
Disulfoton	6.56	Tributyl Phosphate-d27	2.0	0.50	8.0	2.0
Dimethenamid	6.94	Atrazine-d5	0.40	0.10	1.6	0.40
Metribuzin	6.95	Atrazine-d5	0.80	0.20	3.2	0.80
Acetochlor	6.99	Atrazine-d5	1.0	0.25	4.0	1.0
Chlorpyrifos Methyl	7.01	Tributyl Phosphate-d27	0.40	0.10	1.6	0.40
Alachlor	7.08	Atrazine-d5	1.0	0.25	4.0	1.0
Fipronil desulfinyl	7.09	Atrazine-d5	0.50	0.13	2.0	0.50
Ametryn	7.10	Atrazine-d5	1.3	0.33	5.2	1.3
Prometryn	7.13	Atrazine-d5	0.80	0.20	3.2	0.80
Metalaxyl	7.13	Atrazine-d5	1.2	0.30	4.8	1.2
Dithiopyr	7.21	Atrazine-d5	0.40	0.10	1.6	0.40
Prodiamine	7.25	Atrazine-d5	0.70	0.18	2.8	0.70
Parathion Methyl	7.25	Parathion Ethyl-d10	1.0	0.25	4.0	1.0
Bromacil	7.31	Atrazine-d5	2.0	0.50	8.0	2.0

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Malathion	7.35	Tributyl Phosphate-d27	1.0	0.25	4.0	1.0
Metolachlor	7.38	Atrazine-d5	1.0	0. 25	4.0	1.0
Chlorpyrifos Ethyl	7.44	Tributyl Phosphate-d27	0.40	0.10	1.6	0.40
Cyanazine	7.47	Atrazine-d5	2.0	0.50	8.0	2.0
Parathion Ethyl	7.65	Parathion Ethyl-d10	1.0	0.25	4.0	1.0
Pendimethalin	7.70	Parathion Ethyl-d10	4.0	1.0	16	4.0
Fipronil Sulfide	7.72	Tributyl Phosphate-d27	0.60	0.15	2.4	0.60
Fipronil	7.78	Atrazine-d5	1.0	0.25	4.0	1.0
Fenamiphos	8.07	Tributyl Phosphate-d27	1.0	0.25	4.0	1.0
Oxadiazon	8.17	Atrazine-d5	0.40	0.10	1.6	0.40
Fipronil Sulfone	8.25	Tributyl Phosphate-d27	0.60	0.15	2.4	0.60
Ethion	8.49	Tributyl Phosphate-d27	0.60	0.15	2.4	0.60
Norflurazon	8.74	Atrazine-d5	2.0	0.50	8.0	2.0
Hexazinone	8.82	Hexazinone-d6	2.0	0.50	8.0	2.0
Tebuconazole	9.00	Atrazine-d5	2.0	0.50	8.0	2.0
Azinphos Methyl	9.35	Atrazine-d5	9.0	2.3	36	9.0
Tributyl Phosphate- d27	5.51	Internal standard				
Atrazine-d5	6.19	Internal standard				
Parathion Ethyl-d10	7.63	Internal standard				
Hexazinone-d6	8.82	Internal standard				

- *Summary peak is used to report Demeton

TABLE 1A-Soil/Waste: Internal standard associations, MDLs, PQLs and approximate RTs for Nitrogen Phosphorus pesticides included in LIMS test S-PSNP-TQ/WS-PSNP-TQ. **LIMS reporting units are ug/Kg**

Analyte	**Approx. Retention Time (min)**	**Associated internal standard**	**MDL (ug/L)**	**MDL ug/Kg soil**	**MDL (ug/Kg) waste**	**PQL (ug/L)**	**PQL ug/Kg soil**	**PQL (ug/Kg) waste**
			extract	sample	sample	extract	sample	sample
Simazine-d10 surrogate	6.13	Atrazine-d5						
Terbufos-d10 surrogate	6.32	Tributyl Phosphate- d27						
Methamidophos	4.05	Tributyl Phosphate- d27	8.0	0.53	80	32	2.1	320
EPTC	4.30	Atrazine-d5	5.0	0.33	50	20	1.3	200

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Butylate	4.58	Atrazine-d5	4.0	0.27	40	16	1.1	160
Mevinphos	4.64	Tributyl Phosphate- d27	2.0	0.13	20	8.0	0.53	80
Molinate	5.09	Atrazine-d5	1.5	0.10	15	6.0	0.40	60
Demeton*	5.44 –"O" 6.09 - "S"	Tributyl Phosphate- d27	14	0.93	140	56	3.7	560
Ethoprop	5.57	Tributyl Phosphate- d27	0.50	0.033	5.0	2.0	0.13	20
Atrazine Desethyl	5.78	Atrazine-d5	6.0	0.40	60	24	1.6	240
Phorate	5.90	Tributyl Phosphate- d27	1.0	0.067	10	4.0	0.27	40
Monocrotophos	6.06	Tributyl Phosphate- d27	10	0.67	100	40	2.7	400
Simazine	6.17	Atrazine-d5	2.0	0.13	20	8.0	0.53	80
Prometon	6.18	Atrazine-d5	3.6		0.90	14		3.6
Atrazine	6.21	Atrazine-d5	1.0	0.067	10	4.0	0.27	40
Terbuthylazine	6.37	Atrazine-d5	1.0	0.067	10	4.0	0.27	40
Terbufos	6.36	Tributyl Phosphate- d27	0.50	0.033	5.0	2.0	0.13	20
Fonofos	6.41	Tributyl Phosphate- d27	0.80	0.053	8.0	3.2	0.21	3.2
Diazinon	6.49	Atrazine-d5	1.0	0.067	10	4.0	0.27	40
Disulfoton	6.56	Tributyl Phosphate- d27	2.0	0.13	20	8.0	0.53	80
Metribuzin	6.95	Atrazine-d5	2.0	0.13	20	8.0	0.53	80
Acetochlor	6.99	Atrazine-d5	1.0	0.067	10	4.0	0.27	40
Chlorpyrifos Methyl	7.01	Tributyl Phosphate- d27	1.0	0.067	10	4.0	0.27	40
Alachlor	7.08	Atrazine-d5	2.0	0.13	20	8.0	0.53	80
Ametryn	7.10	Atrazine-d5	2.0	0.13	20	8.0	0.53	80
Prometryn	7.13	Atrazine-d5	1.2	0.080	12	4.8	0.32	48
Metalaxyl	7.13	Atrazine-d5	1.2	0.080	12	4.8	0.32	48
Parathion Methyl	7.25	Parathion Ethyl-d10	1.0	0.067	10	4.0	0.27	40
Bromacil	7.31	Atrazine-d5	4.0	0.27	40	16	1.1	160
Malathion	7.35	Tributyl Phosphate- d27	2.0	0.13	20	8.0	0.53	80
Metolachlor	7.38	Atrazine-d5	1.2	0.080	12	4.8	0.32	48
Chlorpyrifos Ethyl	7.44	Tributyl Phosphate- d27	1.0	0.067	10	4.0	0.27	40
Cyanazine	7.47	Atrazine-d5	4.0	0.27	40	16	1.1	160
Parathion Ethyl	7.65	Parathion Ethyl-d10	1.0	0.067	10	4.0	0.27	40

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Pendimethalin	7.70	Parathion Ethyl-d10	4.0	0.27	40	16	1.1	160
Fipronil Sulfide	7.72	Tributyl Phosphate- d27	0.60	0.040	6.0	2.4	0.16	24
Fipronil	7.78	Atrazine-d5	1.0	0.067	10	4.0	0.27	40
Fenamiphos	8.07	Tributyl Phosphate- d27	2.0	0.13	20	8.0	0.53	80
Fipronil Sulfone	8.25	Tributyl Phosphate- d27	0.60	0.040	6.0	2.4	0.16	24
Ethion	8.49	Tributyl Phosphate- d27	1.2	0.080	12	4.8	0.32	48
Norflurazon	8.74	Atrazine-d5	3.0	0.20	30	12	0.80	120
Hexazinone	8.82	Hexazinone-d6	3.0	0.20	30	12	0.80	120
Azinphos Methyl	9.35	Atrazine-d5	5.0	0.33	50	20	1.3	200
Tributyl Phosphate- d27	5.51	Internal standard						
Atrazine-d5	6.19	Internal standard						
Parathion Ethyl-d10	7.63	Internal standard						
Hexazinone-d6	8.82	Internal standard						

- *Summary peak is used to report Demeton

TABLE 1B: Internal standard associations, MDLs, PQLs and approximate RTs for Chlorinated pesticides included in LIMS tests S-PSCL-TQ and WS-PSCL-TQ. **LIMS reporting units are ug/kg**

Analyte	**Approximate Retention Time (min)**	**Associated internal standard**	**MDL ug/L**	**MDL ug/kg soil**	**MDL Ug/kg waste**	**PQL ug/L**	**PQL ug/kg soil**	**PQL ug/kg waste**
			extract	sample	sample	extract	sample	sample
Tetrachloro-m-xylene surrogate	5.99	DCB-d5						
Decachlorobiphenyl surrogate	16.25	HCB-d3						
Trifluralin	6.69	Trifluralin-d14	0.80	0.053	8.0	3.2	0.21	32
Alpha-BHC	6.92	Alpha-BHC-d6	0.50	0.033	5.0	2.0	0.13	20
Beta-BHC	7.42	Alpha-BHC-d6	0.50	0.033	5.0	2.0	0.13	20
Gamma-BHC	7.53	Alpha-BHC-d6	0.50	0.033	5.0	2.0	0.13	20
Delta-BHC	7.94	TCB-d5	0.50	0.033	5.0	2.0	0.13	20
Chlorothalonil	8.04	TCB-d5	2.0	0.13	20	8.0	0.53	80
Heptachlor	8.84	TCB-d5	0.50	0.033	5.0	2.0	0.13	20

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Aldrin	9.52	TCB-d5	1.0	0.067	10	4.0	0.27	40
Heptachlor Epoxide	10.32	TCB-d5	1.0	0.067	10	4.0	0.27	40
Gamma-Chlordane	10.82	TCB-d5	0.50	0.033	5.0	2.0	0.13	20
Endosulfan I	11.07	TCB-d5	2.0	0.13	20	8.0	0.53	80
Alpha-Chlordane	11.13	TCB-d5	0.50	0.033	5.0	2.0	0.13	20
DDE-p,p’	11.60	TCB-d5	0.33	0.022	3.3	1.3	0.088	13
Dieldrin	11.61	HCB-d3	2.0	0.13	20	8.0	0.53	80
Endrin	12.06	HCB-d3	2.0	0.13	20	8.0	0.53	80
Endosulfan II	12.27	HCB-d3	2.0	0.13	20	8.0	0.53	80
DDD-p,p’	12.49	HCB-d3	0.50	0.033	5.0	2.0	0.13	20
Endrin Aldehyde	12.67	HCB-d3	4.0	0.27	40	16	1.1	160
Carbophenothion	13.06	HCB-d3	1.5	0.10	15	6.0	0.40	60
Endosulfan Sulfate	13.18	HCB-d3	1.0	0.067	10	4.0	0.27	40
DDT-p,p’	13.28	DDT-p,p’-d8	1.2	0.080	12	4.8	0.32	48
Endrin Ketone	14.03	HCB-d3	4.0	0.27	40	16	1.1	160
Methoxychlor	14.28	DDT-p,p’-d8	0.50	0.033	5.0	2.0	0.13	20
Mirex	14.73	HCB-d3	1.0	0.067	10	4.0	0.27	40
Permethrin	15.35	HCB-d3	1.2	0.080	12	4.8	0.32	48
Cypermethrin	15.97	HCB-d3	2.5	0.17	25	10	0.67	100
Dicofol-	13.79	Dicofol-d8	1.0	0.067	10	4.0	0.27	40
Trifluralin-d14	6.64	Internal standard						
DCB-d5	6.69	Internal standard						
Alpha-BHC-d6	6.92	Internal standard						
TCB-d5	9.42	Internal standard						
DDT-p,p’-d8	13.30	Internal standard						
Dicofol-d8	13.74	Internal standard						
HCB-d3	14.22	Internal standard						
Octachloronaphthalene	15.80	Internal standard						

TABLE 1C: Internal standard associations, MDLs, PQLs and approximate RTs for typical analytical PCB Aroclors included in LIMS tests S-PCB-TQ and WS-PCB-TQ. **LIMS reporting units are ug/kg**

Analyte	**Approximate Retention Time (min)**	**Associated internal standard**	**RRT**	**matrix**	**MDL ug/L**	**MDL ug/kg**	**PQL ug/L**	**PQL ug/kg**
					extract	sample	extract	sample
Decachlorobiphenyl surrogate	16.25	HCB-d3	1.13					
PCB-1016				s	10	0.67	40	2.7
PCB-1016				ws	10	100	40	400
PCB-1016_1	6.33	DCB-d5	0.95					

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PCB-1016_2	6.96	DCB-d5	1.04					
PCB-1016_3	8.02	TCB-d5	0.85					
PCB-1016_4	8.71	TCB-d5	0.93					
PCB-1016_5	9.60	TCB-d5	1.02					
PCB-1221				s	10	0.67	40	2.7
PCB-1221				ws	10	100	40	400
PCB-1221_1	5.51	DCB-d5	0.82					
PCB-1221_2	6.02	DCB-d5	0.90					
PCB-1221_3	6.32	DCB-d5	0.95					
PCB-1221_4	6.86	DCB-d5	1.03					
PCB-1221_5	6.96	DCB-d5	1.04					
PCB-1232				s	10	0.67	40	2.7
PCB-1232				ws	10	100	40	400
PCB-1232_1	6.33	DCB-d5	0.95					
PCB-1232_2	6.97	DCB-d5	1.04					
PCB-1232_3	8.02	TCB-d5	0.85					
PCB-1232_4	8.72	TCB-d5	0.93					
PCB-1232_5	9.61	TCB-d5	1.02					
PCB-1242				s	10	0.67	40	2.7
PCB-1242				ws	10	100	40	400
PCB-1242_1	6.32	DCB-d5	0.95					
PCB-1242_2	6.96	DCB-d5	1.04					
PCB-1242_3	8.02	TCB-d5	0.85					
PCB-1242_4	8.50	TCB-d5	0.90					
PCB-1242_5	8.85	TCB-d5	0.94					
PCB-1248				s	10	0.67	40	2.7
PCB-1248				ws	10	100	40	400
PCB-1248_1	8.02	DCB-d5	1.20					
PCB-1248_2	8.51	DCB-d5	1.27					
PCB-1248_3	9.60	TCB-d5	1.02					
PCB-1248_4	10.40	TCB-d5	1.10					
PCB-1248_5	10.48	TCB-d5	1.11					
PCB-1254				s	10	0.67	40	2.7
PCB-1254				ws	10	100	40	400
PCB-1254_1	9.60	TCB-d5	1.02					
PCB-1254_2	10.39	TCB-d5	1.10					
PCB-1254_3	11.72	TCB-d5	1.25					
PCB-1254_4	12.26	TCB-d5	1.30					
PCB-1254_5	13.34	HCB-d3	0.93					
PCB-1260				s	10	0.67	40	2.7

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PCB-1260				ws	10	100	40	400
PCB-1260_1	12.24	TCB-d5	1.30					
PCB-1260_2	12.76	TCB-d5	1.36					
PCB-1260_3	13.69	HCB-d3	0.95					
PCB-1260_4	14.06	HCB-d3	0.98					
PCB-1260_5	14.20	HCB-d3	0.98					
DCB-d5	6.68	Internal standard						
TCB-d5	9.40	Internal standard						
HCB-d3	14.42	Internal standard						

TABLE 1D: Internal standard associations, MDLs, PQLs and approximate RTs for Chlorinated pesticides and PCB congeners included in LIMS test T-PCBCL-TQ. **LIMS reporting units are ug/kg**

Analyte	**Approximate Retention Time (min)**	**Associated internal standard**	**MDL ug/L**	**MDL ug/kg**	**PQL ug/L**	**PQL ug/kg**
			extract	sample	extract	sample
Tetrachloro-m-xylene	5.99	HCB-d3				
Decachlorobiphenyl surrogate	15.79	HCB-d3				
Alpha-BHC	6.57	Alpha-BHC-d6	0.50	0.20	2.0	0.80
Hexachlorobenzene	6.70	DCB-d5	1.0	0.40	4.0	1.6
Beta-BHC	6.99	Alpha-BHC-d6	0.80	0.32	3.2	1.3
Gamma-BHC	7.09	Alpha-BHC-d6	0.50	0.20	2.0	0.80
Delta-BHC	7.48	TCB-d5	0.80	0.32	3.2	1.3
Heptachlor	8.33	TCB-d5	0.80	0.32	3.2	1.3
Aldrin	8.97	TCB-d5	1.0	0.40	4.0	1.6
Heptachlor Epoxide	9.75	TCB-d5	1.0	0.40	4.0	1.6
Trans-Chlordane	10.23	TCB-d5	1.0	0.40	4.0	1.6
DDE-o,p’	10.37	TCB-d5	0.50	0.20	2.0	0.80
Endosulfan I	10.47	TCB-d5	2.0	0.80	8.0	3.2
Cis-Chlordane	10.54	TCB-d5	1.0	0.40	4.0	1.6
Trans-Nonachlor	10.64	TCB-d5	2.0	0.80	8.0	3.2
DDE-p,p’	11.02	TCB-d5	0.50	0.20	2.0	0.80
Dieldrin	11.01	HCB-d3	2.0	0.80	8.0	3.2
DDD-o,p’	11.19	HCB-d3	0.50	0.20	2.0	0.80
Endrin	11.44	HCB-d3	2.0	0.80	8.0	3.2
Endosulfan II	11.65	HCB-d3	2.0	0.80	8.0	3.2

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DDD-p,p’	11.89	HCB-d3	1.0	0.40	4.0	1.6
Cis-Nonachlor	11.94	HCB-d3	2.0	0.80	8.0	3.2
DDT-o,p’	11.95	DDT-p,p’-d8	1.0	0.40	4.0	1.6
Endrin Aldehyde	12.05	HCB-d3	2.0	0.80	8.0	3.2
Endosulfan Sulfate	12.56	HCB-d3	1.0	0.40	4.0	1.6
DDT-p,p’	12.68	DDT-p,p’-d8	1.0	0.40	4.0	1.6
Endrin Ketone	13.52	HCB-d3	2.0	0.80	8.0	3.2
Methoxychlor	13.88	DDT-p,p’-d8	2.0	0.80	8.0	3.2
Mirex	14.34	HCB-d3	1.0	0.40	4.0	1.6
PCB-8	6.57	DCB-d5	1.0	0.40	4.0	1.6
PCB-18	7.25	DCB-d5	1.0	0.40	4.0	1.6
PCB-28	8.05	TCB-d5	0.80	0.32	3.2	1.3
PCB-52	8.69	TCB-d5	2.0	0.80	8.0	3.2
PCB-44	9.09	TCB-d5	0.50	0.20	2.0	0.80
PCB-66	9.93	TCB-d5	0.50	0.20	2.0	0.80
PCB-101	10.42	TCB-d5	0.50	0.20	2.0	0.80
PCB-77	11.16	HCB-d3	0.50	0.20	2.0	0.80
PCB-118	11.70	HCB-d3	0.50	0.20	2.0	0.80
PCB-153	12.18	HCB-d3	0.50	0.20	2.0	0.80
PCB-105	12.26	HCB-d3	0.50	0.20	2.0	0.80
PCB-138	12.76	HCB-d3	0.50	0.20	2.0	0.80
PCB-126	12.94	HCB-d3	0.50	0.20	2.0	0.80
PCB-187	13.11	HCB-d3	0.80	0.32	3.2	1.3
PCB-128	13.33	HCB-d3	0.80	0.32	3.2	1.3
PCB-180	14.04	HCB-d3	0.80	0.32	3.2	1.3
PCB-169	14.30	HCB-d3	0.50	0.20	2.0	0.80
PCB-170	14.41	HCB-d3	0.80	0.32	3.2	1.3
PCB-195	14.87	HCB-d3	0.80	0.32	3.2	1.3
PCB-206	15.46	HCB-d3	0.80	0.32	3.2	1.3
DCB-d5	6.30	Internal standard				
Alpha-BHC-d6	6.52	Internal standard				
TCB-d5	8.88	Internal standard				
DDT-p,p’-d8	12.62	Internal standard				
HCB-d3	13.78	Internal standard				

TABLE 1E: Internal standard associations, MDLs, PQLs and approximate RTs for Chlorinated pesticides included in LIMS W-DIELDRIN. **LIMS reporting units are ng/L.**

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Analyte	**Approximate Retention Time (min)**	**Associated internal standard**	**MDL ug/L**	**MDL ng/L**	**PQL ug/L**	**PQL ng/L**
			extract	sample	extract	sample
Tetrachloro-m-xylene surrogate	5.16	DCB-d5				
Decachlorobiphenyl surrogate	9.07	HCB-d3				
Dieldrin	7.24	HCB-d3	0.80	0.40	3.2	1.6
DCB-d5	5.30	Internal standard				
HCB-d3	7.81	Internal standard				

TABLE 2: GC/MS Operating Conditions: (METHOD CL_MRM_yymmdd, AR-MRM-yymmdd) and Cl_T_MRM-yymmdd

Parameter	**Setting**
Mass spec:	70 eV. Peak width 0.7s. detector setting-gain. Source temp. 300 C. Collision cell He: 2.25 mL/min, Nitrogen 1.5 mL/min.
Scan Time:	About 3.3 cycles/s. MRM mode dwell times variable, summing up to about 300 ms per time segment. Gain 20 for each transition monitored for most analytes. Gain 10 is used for PCB aroclors and the tissue method. Time filtering “on”.
GC Oven Temperature Program:	50 °C for 1.5 min, to 160 °C at 55 C °/min, hold 0 min, to 240 C at 8 C/min hold 0 min, to 280 °C at 50 C °/min, hold 0 min, to 290 at 100 C °/min hold 3 min (7 min for chlorinated pesticides in soil, AR and tissue methods). This program is the same for full scan (used for RT shifts determination and degradation mix analysis) or MRM.
Injector operating conditions:	Temp: 60 °C for 0.35 min; 900 C °/min to 280 C. hold for 14 min, 900 C °/min to 310 hold until end run. Mode: pulsed splitless; pulse pressure 30 PSI for 1.4 min after pulse pressure: Ramped Flow ON, 2.8154 psi at 60 °C (0.8 mL/min) for NP method or 3.3217 psi at 60 °C (0.9 mL/min) for CL, T_CL and AR methods ; cryo: ON (nitrogen gas); Cryo use temperature 150 °C
Column 1 configuration	HP-5MS UI, 5m-0.25mm-0.25um; in: front MMI inlet, out aux EPC 4 (EPC 6 in TQ-2)
Column 1 flow CL CL_T and AR methods	0.9 ml/min for 17 min, then at 100 mL/min to -2.5 mL/min for 1.5 min, then at 100 mL/min to -5 mL/min for until end run
Column 2 configuration	HP-5MS UI, 15m-0.25mm-0.25um; in: t aux EPC 4 (EPC 6 in TQ-2); out: vacuum
Column 2 flow CL CL_T and AR methods	1.0 ml/min for 18.53 min, then at 100 mL/min to 2.4 mL/min until end run
MS interface temperature:	300 °C
Injection Type:	Pulsed Splitless (cold). Pulse pressure 30 PSI for 1.4 min; purge to split vent 50 mL/min at 1.5 min. Gas saver OFF.

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Injection Volume:	2 µL
Backflash:	Concurrent + end run; see columns flows conditions
Total Run Time CL CL_T and AR methods	21.40 min.

TABLE 2-B: GC/MS Operating Conditions: (METHOD DIELDRIN_MRM-yymmdd and DIELDRIN_SPE_yymmdd)

Parameter	Setting
Mass spec:	70 eV. Peak width 0.7s. detector setting-gain. Source temp. 300 C. Collision cell He: 2.25 mL/min, Nitrogen 1.5 mL/min.
Scan Time:	About 3.3 cycles/s. MRM mode dwell times variable, summing up to about 300 ms per time segment. Gain 20 for each transition monitored for most analytes. Time filtering “on”
GC Oven Temperature Program:	60 °C for 1.5 min, to 200 °C at 50 C °/min, hold 0 min, to 230 C at 20 C/min hold 0 min, to 300 °C at 50 C °/min, hold 5.5 min,).
Injector operating conditions:	Temp: 60 °C for 0.35 min; 900 C °/min to 280 C. hold for 11 min, 900 C °/min to 310 hold until end run. Mode: pulsed splitless; pulse pressure 30 PSI for 1.4 min after pulse pressure: Ramped Flow ON, 2.8 psi at 60 °C (0.8 mL/min) cryo: ON (nitrogen gas); Cryo use temperature 150 °C
Column 1 configuration	HP-5MS UI, 5m-0.25mm-0.25um; in: front MMI inlet, out aux EPC 4 (EPC 6 in TQ-2)
Column 1 flow	0.8 ml/min for 8.3 min, then at 100 mL/min to -2.5 mL/min for 1.5 min, then at 100 mL/min to -5 mL/min for until end run
Column 2 configuration	HP-5MS UI, 15m-0.25mm-0.25um; in: t aux EPC 4 (EPC 6 in TQ-2); out: vacuum
Column 2 flow	0.9 ml/min for 9.83 min, then at 100 mL/min to 2.4 mL/min until end run
MS interface temperature:	300 °C
Injection Type:	Pulsed Splitless (cold). Pulse pressure 30 PSI for 1.4 min; purge to split vent 50 mL/min at 1.5 min. Gas saver OFF.
Injection Volume:	2 µL
Backflash:	Concurrent + end run; see columns flows conditions
Total Run Time NP method:	12.7 min.

TABLE 2-C: GC/MS Operating Conditions: METHOD NP_MRM-yymmdd MRM-yymmdd

Parameter	Setting
Mass spec:	70 eV. Peak width 0.7s. detector setting-gain. Source temp. 300 C. Collision cell He: 2.25 mL/min, Nitrogen 1.5 mL/min.

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Scan Time:	About 3.3 cycles/s. MRM mode dwell times variable, summing up to about 300 ms per time segment. Gain 20 for each transition monitored for most analytes. Time filtering “on”.
GC Oven Temperature Program:	50 °C for 1.5 min, to 160 °C at 55 C °/min, hold 0 min, to 200 C at 13 C/min hold 0 min, to 280 °C at 55 C °/min, hold 0 min, to 290 at 100 C °/min hold 5.9 min.
Injector operating conditions:	Temp: 60 °C for 0.35 min; 900 C °/min to 280 C. hold for 14 min, 900 C °/min to 310 hold until end run. Mode: pulsed splitless; pulse pressure 30 PSI for 1.4 min after pulse pressure: Ramped Flow ON, 4.4394 psi at 60 °C (1.1 mL/min) cryo: ON (nitrogen gas); Cryo use temperature 150 °C
Column 1 configuration	HP-5MS UI, 5m-0.25mm-0.25um; in: front MMI inlet, out aux EPC 4 (EPC 6 in TQ-2)
Column 1 flow NP method	1.1 ml/min for 9.5 min, then at 100 mL/min to -2.5 mL/min for 1.5 min, then at 100 mL/min to -5 mL/min for until end run
Column 2 configuration	HP-5MS UI, 15m-0.25mm-0.25um; in: t aux EPC 4 (EPC 6 in TQ-2); out: vacuum
Column 2 flow NP method	1.2 ml/min for 11.036 min, then at 100 mL/min to 2.4 mL/min until end run
MS interface temperature:	300 °C
Injection Type:	Pulsed Splitless (cold). Pulse pressure 30 PSI for 1.4 min; purge to split vent 50 mL/min at 1.5 min. Gas saver OFF.
Injection Volume:	2 µL
Backflash:	Concurrent + end run; see columns flows conditions
Total Run Time NP method:	14.03 min.

TABLE 3: GC AUTOSAMPLER OPERATING PARAMETERS FOR GC/MS/MS ANALYSIS

Autosampler Parameter	**Setting**
Syringe size	10 uL
Injection volume	2 uL
Last Bottle	150
Solvent A washes	3 pre- 15 post (DI Water)
Solvent A volume	8 uL
Solvent B washes	3 pre- 15 post (Acetone)
Solvent B volume	8 uL
Sample washes	1
Sample wash volume	4 uL
Sample pumps	7
Dwell time pre-inj	0
Dwell time post-inj	0

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Solvent wash draw speed	300 uL/min
Solvent wash dispense speed	6000 uL/min
Sample wash draw speed	50 uL/min
Sample wash dispense speed	6000 uL/min
Injection dispense speed	68uL/min
Viscosity delay	7 sec
Sample depth	disabled
Injection type	3-layer Sandwich
L1 airgap	0.0 uL
L2 Volume	0.2 uL MeOH
L2 airgap	0.0 uL
L3 Volume	0.4 uL analyte protectants
L3 airgap	0.0 uL
Sample overlap	Not enabled

TABLE 4A. MRM method acquisition parameters for Nitrogen-Phosphorus pesticides (ref 15.14)

Analyte	**Time segment /time segment start time**	**Quantifier transitions**	**Collision energy (V) quant**	**Qualifier transition**	**Collision energy (V) qual**
EPTC	TS1/3.75	189.1-128.1	5	128.1-86.1	5
Butylate	TS1/3.75	217.1-156.1	5	174.1-146.1	10
Mevinphos	TS1/3.75	192-127	10	127-95	15
Molinate	TS1/3.75	187-126	5	187-158	9
Demeton-O	TS2/5.32	171.0-115	10	171.0-97	25
Tributyl Phosphate- d27	TS2/5.32	103.1-83	20	103.1-63	37
Ethoprop	TS2/5.32	158-97	15	158-114	5
Atrazine Desethyl	TS2/5.32 TS3/5.99	186.9-172.1	5	145.0-110.1 187.0-110.1	10 21
Phorate	TS2/5.32 TS3/5.99	231-174.9	15	231-128.9	15
Demeton-S	TS3/5.99	171-115	10	171-97	25
Simazine-d10	TS3/5.99 TS4/6.30	211.3-179.1	3	179.2-144	5
Simazine	TS3/5.99 TS4/6.30	185.6-90.9	9	201.1-138.1	15 15
Prometon	TS3/5.99 TS4/6.30	225.2-183.1	10	225.2-210.2	10
Atrazine-d5	TS3/5.99	205.1-105.1	15	205.1-127.1	10
Atrazine	TS3/5.99	200.1-104	20	200.1-122.1	10

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	TS4/6.30				
Terbuthylazine	TS4/6.30	213.9-104	20	213.9-132	10
Terbufos-d10	TS4/6.30	241.1-130.9	25	163.0-98.9	13
Terbufos	TS4/6.30	231.0-128.9	25	213-174.9	10
Fonofos	TS4/6.30	246-137	10	246-109	18
Diazinon	TS4/6.30	304.1-179.1	10	179.1-121.1	40
Disulfoton	TS4/6.30	185.9-108.9	7	185.9-97	17
Dimethenamid	TS5/6.77	230-154	9	154-111	13
Metribuzin	TS5/6.77	198-82	15	198-55	30
Acetochlor	TS5/6.77	223-132	21	223-147.1	7
Chlorpyrifos Methyl	TS5/6.77	286-93	30	286-270.9	30
Alachlor	TS5/6.77	188.1-160.1	10	161.1-146.1	12
Fipronil Desulfinyl	TS5/6.77	387.9-332.9	18	387.9-280.9	35
Ametryn	TS5/6.77	227.1-58.3	30	227.1-155.2	30
Prometryn	TS5/6.77 TS6/7.22	241.1-58.2	30	241.1-184.2	30
Metalaxyl	TS5/6.77	234.1-174.1	10	249.1-190.1	10
Dithiopyr	TS5/6.77	354.1-306	5	354.1-286	13
Prodiamine	TS5/6.77	321.0-279.0	4	321.0-203.0	13
Parathion Methyl	TS5/6.77	262.9-109.0	10	262.9-124.9	15
Bromacil	TS6/7.22	205-132	30	231-188	7
Malathion-d7	TS6/7.22	163.9-130.0	5	217.9-130.9	10
Malathion	TS6/7.22	173.1-99.0	15	173.1-117	10
Chlorpyrifos Ethyl	TS6/7.22	196.9-168.9	15	196.9-07	40
Metolachlor	TS6/7.22	162.1-133.1	15	238-162	10
Cyanazine	TS6/7.22	225.1-198.1	10	225.1-189.1	10
Parathion Ethyl-d10	TS6/7.22	301.0-115.0	20	301-147	4
Parathion Ethyl	TS6/7.22	291.0-109.0	15	291.0-137.0	10
Pendimethalin	TS6/7.22 TS7/7.63	252.1-162.1	15	252.1-191.1	8
Fipronil Sulfide	TS7/7.63	350.9-255	15	419.9-351	10
Fipronil	TS7/7.63	367-213	20	367-255	15
Fenamiphos	TS7/7.63	154-139	10	303-195	5
Oxadiazon	TS7/7.63	174.9-112	15	301.9-175.0	13
Fipronil Sulfone	TS7/7.63	382.9-255	20	255-228	10
Ethion	TS8/8.39	231.0-128.9	25	231-174.9	10
Norflurazon	TS8/8.39	303.3-145	21	303.3-173.1	8
Hexazinone-d6	TS8/8.39	177.2-77.1	15	177.2-91.1	12
Hexazinone	TS8/8.39	171.1-85.1	15	128-83	12
Tebuconazole	TS8/8.39	250.0-125.0	27	252.0-127.0	25

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Azinphos Methyl	TS8/8.39	160.1-77.1	20	160.1-132.1	0

TABLE 4B. MRM method acquisition parameters for Chlorinated pesticides (soil mix) (ref 15.14)

Analyte	**Time segment /time segment start time**	**Quantifier transitions**	**Collision energy (V) quant**	**Qualifier transition**	**Collision energy (V) qual**
Tetrachloro-m-xylene	TS1/3.76	206.9 - 136	20	206.9 - 171.9	27
Trifluralin-d14	TS1/3.76	315-267.1	7	266.9-163.1	17
Trifluralin	TS1/3.76	306.1-264.0	5	306.1-160.0	30
DCB-d5	TS1/3.76	226.9-157.1	28	226.9-192.1	12
Alpha-BHC-d6	TS1/3.76	223.8-187.0	8	223.8-150	23
Alpha-BHC	TS1/3.76	181.0-145.0	15	181.0-109.0	30
Beta-BHC	TS2/7.19	181.0-145.0	15	181.0-109.0	30
Gamma-BHC	TS2/7.19	181.0-145.0	15	181.0-109.0	30
Delta-BHC	TS3/7.89	181.0-145.0	15	181.0-109.0	30
Chlorothalonil	TS3/7.89	265.9-230.9	20	265.9-133.0	40
Heptachlor	TS4/8.41	271.9-236.8	25	271.9-234.8 273.9-239.1* 273.9-236.8*	14 25 25
TCB-d5	TS5/9.33	296.8-225.0	28	296.8-262.0	12
Aldrin	TS5/9.33	260.9-190.9	40	262.9-190.9 262.9-192.9	40 40
Heptachlor Epoxide	TS5/9.33	352.9-262.8	15	352.9-281.9 354.8-264.9*	16 15
Gamma-Chlordane	TS6/10.63	271.7-236.9	12	372.9-263.9	20
Endosulfan I	TS6/10.63	240.9-205.9	15	206.8-172.0 240.0-205.0	13 15
Alpha-Chlordane	TS6/10.63	271.7-236.9	12	372.9-263.9	20
DDE-p,p’	TS7/11.48	246.0-176.1	40	246.0-175.1	40
Dieldrin	TS7/11.48	262.9-192.9	40	262.9-190.9 276.9-240.9* 260.9-190.9	35 10 35
Endrin	TS8/11.91	262.8-192.8	30	262.7-191.1 316.8-280.9* 280.9-244.9	40 6 5

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Endosulfan II	TS8/11.91	241.0-206.0	15	195.0-159.0 206.9-172.1	10 14
DDD-p,p’	TS8/11.91	235.0-165.1	25	235.0-199.1	20
Endrin Aldehyde	TS8/11.91	344.8-280.9	6	344.8-244.9 346.8-282.9 346.8-280.9*	10 6 6
Carbophenothion	TS9/12.90	341.9-157.0	13	157.0-121.0 343.9-158.9 342-143*	25 13 25
Endosulfan Sulfate	TS9/12.90	271.7-236.8	12	273.7-236.9 269.7-234.9 386.8-288.7*	12 12 5
DDT-p,p’	TS9/12.90	235.0-165.1	30	235.0-199.1	20
DDT-p,p’-d8	TS9/12.90	243.0-172.6	20	243.0-206.1	15
Endrin Ketone	TS10/13.65	316.9-280.9	7	316.9-101.1 314.8-278.8*	14 7
HCB-d3	TS10/13/65	362.7-362.7	5	362.7-292.9	32
Methoxychlor	TS10/13.65	227.1-169.1	30	227.1-141.1 227-212*	40 15
Mirex	TS10/13.65	271.9-236.9	15	271.9-234.8	14
Dicofol-d8	TS11/15.05	142.9-115.1	15	142.9-78	34
Dicofol-	TS11/15.05	251-139	15	253-141	15
Permethrin	TS11/15.05	183.1-168.1	15	183.1-153.1	15
Cypermethrin	TS11/15.05	180.9-152.1	23	208.9-169.2	11
Decachlorobiphenyl	TS11/15.05	497.6-427.9	20	497.6-462.7	15

- ***** transitions not used for quantitation. Only used for additional confirmations.

TABLE 4C-1. MRM method acquisition parameters for PCB aroclors (all in one time segment)

Compound Name	Precursor Ion	MS1 resolution	Product Ion	MS2 resolution	Dwell (ms)	CE (V)
Decachlorobiphenyl	497.6	Unit	462.7	Wide	11	15
Decachlorobiphenyl	497.6	Unit	427.9	Wide	11	20
Nonachlorobiphenyl	461.7	Unit	391.8	Wide	11	25

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Octachlorobiphenyl	427.8	Unit	357.8	Wide	11	25
Heptachlorobiphenyl-2	393.8	Unit	358.7	Wide	11	12
Heptachlorobiphenyl	393.8	Unit	323.9	Wide	11	25
HCB-d3-ISTD	362.7	Unit	292.9	Wide	11	32
HCB-d3-ISTD	362.7	Unit	362.7	Wide	11	5
Hexachlorobiphenyl-2	359.8	Unit	324.9	Wide	11	11
Hexachlorobiphenyl	359.8	Unit	289.9	Wide	11	25
Pentachlorobiphenyl	325.9	Unit	255.9	Wide	11	25
Pentachlorobiphenyl-2	325.9	Unit	291	Wide	11	10
Pentachlorobiphenyl-3	325.9	Unit	253.9	Wide	11	18
TCB-d5-ISTD	296.8	Unit	225	Wide	11	28
TCB-d5-ISTD	296.8	Unit	262	Wide	11	12
Tetrachlorobiphenyl	291.9	Unit	222	Wide	11	25
Tetrachlorobiphenyl-2	291.9	Unit	220.1	Wide	11	22
Tetrachlorobiphenyl-3	288	Unit	153.1	Wide	11	14
Trichlorobiphenyl	258	Unit	186	Wide	11	25
Trichlorobiphenyl-2	255.8	Unit	185.9	Wide	11	21
DCB-d5-ISTD	226.9	Unit	157.1	Wide	11	28
DCB-d5-ISTD	226.9	Unit	192.1	Wide	11	12
Dichlorobiphenyl-2	222	Unit	187.1	Wide	11	9
Dichlorobiphenyl	222	Unit	152	Wide	11	25
Dichlorobiphenyl-3	219.8	Unit	149.7	Wide	11	26
Monochlorobiphenyl	188	Unit	152	Wide	11	25
Monochlorobiphenyl-2	153.9	Unit	115.2	Wide	11	22
Monochlorobiphenyl-3	153.9	Unit	128	Wide	11	18

*Some transitions are not found in any of the quantitation methods. They are only used for pattern recognition.

TABLE 4C-2. Quantifier and Qualifier MRM transitions for analytical PCB aroclors peaks.

Analyte	**Quantifier transitions**	**Collision energy (V) quant**	**Quantifier's Transition name in the acquisition method**	**Qualifier transition**	**Collision energy (V) qual**	**Qualifier's transition name in the acquisition method**
DCB-d5 istd	226.9-157.1	28	DCB-d5	226.9-192.1	12	DCB-d5
TCB-d5 istd	296.8-225	28	TCB-d5	296.8-262	12	TCB-d5
HCB-d3 istd	362.7-362.7	5	HCB-d3	362.7-292.9	32	HCB-d3

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Decachlorobiphenyl surrogate	497.6-427.9	20	Decachlorobiphenyl	497.6-462.7	15	Decachlorobiphenyl
PCB-1016_1	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1016_2	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1016_3	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1016_4	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1016_5	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2
PCB-1221_1	188.0-152.0	25	Monochlorobiphenyl			
PCB-1221_2	188.0-152.0	25	Monochlorobiphenyl			
PCB-1221_3	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1221_4	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1221_5	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1232_1	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1232_2	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1232_3	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1232_4	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1232_5	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2
PCB-1242_1	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1242_2	222.0-152.0	25	Dichlorobiphenyl	222.0-187.1	9	Dichlorobiphenyl-2
PCB-1242_3	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1242_4	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1242_5	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1248_1	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1248_2	255.8-185.9	21	Trichlorobiphenyl-2	258.0-186	25	Trichlorobiphenyl
PCB-1248_3	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2
PCB-1248_4	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2
PCB-1248_5	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2
PCB-1254_1	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2

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PCB-1254_2	291.9-222.0	25	Tetrachlorobiphenyl	291.9-220.1	22	Tetrachlorobiphenyl-2
PCB-1254_3	325.9-255.9	25	Pentachlorobiphenyl	325.9-253.9	18	Pentachlorobiphenyl-3
PCB-1254_4	325.9-255.9	25	Pentachlorobiphenyl	325.9-253.9	18	Pentachlorobiphenyl-3
PCB-1254_5	359.8-289.9	25	Hexachlorobiphenyl	359.8-324.9	11	Hexachlorobiphenyl-2
PCB-1260_1	359.8-289.9	25	Hexachlorobiphenyl	359.8-324.9	11	Hexachlorobiphenyl-2
PCB-1260_2	359.8-289.9	25	Hexachlorobiphenyl	359.8-324.9	11	Hexachlorobiphenyl-2
PCB-1260_3	393.8-323.9	25	Heptachlorobiphenyl	393.8-358.7	12	Heptachlorobiphenyl-2
PCB-1260_4	393.8-323.9	25	Heptachlorobiphenyl	393.8-358.7	12	Heptachlorobiphenyl-2
PCB-1260_5	393.8-323.9	25	Heptachlorobiphenyl	393.8-358.7	12	Heptachlorobiphenyl-2

TABLE 4D. MRM method acquisition parameters for Chlorinated pesticides (tissue mix) (ref 15.14)

Analyte	Time segment/ TS start time	Quant Transition	Collision energy (V) quant	Qual Transition	Collision energy (V) qual
Tetrachloro-m-xylene	TS1/6.00	206.9 - 136	20	206.9 - 171.9	27
PCB-8	TS2/6.50	222 - 152	25	223.9 - 152	25
Alpha-BHC	TS2/6.50	181 - 145	15	181 - 109	30
Hexachlorobenzene	TS2/6.50	283.7 - 248.8	23	283.7 - 213.9	35
DCB-d5	TS2/6.50	226.9-157.1	28	226.9-192.1	12
Alpha-BHC-d6	TS2/6.50	223.8-187.0	8	223.8-150.0	23
Gamma-BHC	TS3/7.26	181 - 145	15	181 - 109	30
Beta-BHC	TS3/7.26	181 - 145	15	181 - 109	30
PCB-18	TS3/7.26	255.8 - 186	25	258 - 186	25
Delta-BHC	TS3/7.26	181 - 145	15	181 - 109	30
PCB-28	TS4/8.25	255.8 - 186	25	258 - 186	25
Heptachlor	TS4/8.25	271.9 - 236.8	25	271.9 - 234.8 Area sum 273.9-239.1* 273.9-236.8*	14 25 25
PCB-52	TS5/9.00	291.9 - 222	25	219.8 - 149.7	26
TCB-d5	TS5/9.00	296.8-225.0	28	296.8-262	12
Aldrin	TS5/9.00	262.9 - 192.9	40	262.9 - 190.9	40
				260.9 - 190.9 Area sum	40
PCB-44	TS5/9.00	291.9 - 222	25	219.8 - 149.7	26
Heptachlor Epoxide	TS6/10.00	352.9 - 262.8	15	352.9 - 281.9 Area sum 354.8-264.9*	16 16

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PCB-66	TS6/10.00	291.9 - 222	25	219.8 - 149.7	26
Trans-Chlordane	TS7/10.65	372.9 - 263.9	20	271.7-236.9	12
DDE-o,p'	TS7/10.65	246 - 176.1	40	246 - 175.1	40
PCB-101	TS7/10.65	325.9 - 255.9	25	325.9 - 253.9	18
Endosulfan I	TS7/10.65	240.9 - 205.9	15	206.8 - 172	13
				240 – 205 Area sum	15
Cis-Chlordane	TS7/10.65	372.9 - 263.9	20	271.7-236.9	12
Trans-Nonachlor	TS7/10.65	408.7 - 299.8	19	408.7 - 372.7	10
Dieldrin	TS8/11.35	262.9 - 190.9	35	262.9 - 192.9	40
				276.9 - 240.9	10
				260.9 - 190.9 Area sum	35
DDE-p,p'	TS8/11.35	246 - 176.1	40	246 - 175.1	40
PCB-77	TS8/11.35	291.9 - 222	25	219.8 - 149.7	26
DDD-o,p'	TS8/11.35	235 - 165.1	25	235 - 199.1	20
Endrin	TS9/11.87	262.8 - 192.8	30	262.7 - 191.1	40
				280.9 - 244.9	5
				316.8 - 280.9* Area sum	6
Endosulfan II	TS10/12.07	206.9 - 172.1	14	195 - 159	10
				241 – 206 Area sum	15
PCB-118	TS10/12.07	325.9 - 255.9	25	325.9 - 253.9	18
DDD-p,p'	TS10/12.07	235 - 165.1	25	235 - 199.1	20
Cis-Nonachlor	TS11/12.33	408.7 - 372.7	10	408.7 - 299.8	19
DDT-o,p'	TS11/12.33	235 - 165.1	25	235 - 199.1	20
Endrin Aldehyde	TS11/12.33	344.8 - 280.9	6	344.8 - 244.9	10
				346.8 - 282.9	6
				346.8 - 280.9 Area sum	6
PCB-153	TS11/12.33	359.8 - 289.9	25	359.8 - 324.9	11
PCB-105	TS11/12.33	325.9 - 255.9	25	325.9 - 253.9	18
Endosulfan Sulfate	TS12/12.98	271.7 - 236.8	12	273.7 - 236.9	12
				269.7 - 234.9	12
				386.8 - 288.7* Area sum	5
DDT-p,p'	TS12/12.98	235 - 165.1	30	235 - 199.1	20
DDT-p,p'-d8	TS12/12.98	243-206.1	15	243-172.6	20
PCB-138	TS13/13.37	359.8 - 289.9	25	359.8 - 324.9	11
PCB-126	TS13/13.37	325.9 - 255.9	25	325.9 - 253.9	18
PCB-187	TS13/13.37	393.8 - 323.9	25	393.8 - 358.7	12
PCB-128	TS14/13.74	359.8 - 289.9	25	359.8 - 324.9	11
Endrin Ketone	TS14/13.74	316.9 - 280.9	7	316.9 - 101.1 Area sum 314.8-278.8*	14 7
Methoxychlor	TS15/14.06	227.1 - 169.1	30	227.1 - 141.1 Area sum 227.1-212*	40 15
HCB-d3	TS15/14.06	362.7-362.7	5	362.7-292.9	32

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PCB-180	TS15/14.06	393.8 - 323.9	25	393.8 - 358.7	12
PCB-169	TS16/14.51	359.8-289.9	25	359.8-324.9	11
Mirex	TS16/14.51	271.9 - 236.9	15	271.9 - 234.8	14
PCB-170	TS16/14.51	393.8 - 323.9	25	393.8 - 358.7	12
PCB-195	TS17/14.98	429.6 - 394.8	15	392.7 - 357.9	15
PCB-206	TS18/15.55	463.6 - 428.8	15	463.6 - 393.9	34
Decachlorobiphenyl	TS18/15.55	497.6 - 427.9	20	497.6 - 462.7	15

TABLE 4E. MRM method acquisition parameters for Chlorinated pesticides in water -dieldrin only (ref 15.14), test: W-DIELDRIN

Analyte	**Time segment /time segment start time**	**Quantifier transitions**	**Collision energy (V) quant**	**Qualifier transition**	**Collision energy (V) qual**
Tetrachloro-m-xylene	TS1/3.84	206.9 - 136	20	206.9 - 171.9	27
DCB-d5	TS1/3.84	226.9-157.1	28	226.9-192.1	12
Dieldrin (W-DIELDRIN)	TS2/5.97	276.9-240.9	10	345.0-263.0	15
HCB-d3	TS3/7.50	362.7-362.7	5	362.7-292.9	32
Decachlorobiphenyl	TS3/7.50	497.6-427.9	20	497.6-462.7	15

Table 5A: Analyte concentrations in calibration standards for Nitrogen Phosphorus pesticides (ug/L). The expected spike concentrations in LFBs/MSs are 80% of L-5 whereas in the CCV and ICV are equal to L5

ANALYTE	L8	L7	L6	L5	L4	L3	L2	L1	ICV	spk
NPTQ MIX	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Acetochlor	200	100	50	20	10	4	2	1	20	80
Alachlor	600	300	150	60	30	12	6	3	60	240
Ametryn	200	100	50	20	10	4	2	1	20	80
Atrazine	200	100	50	20	10	4	2	1	20	80
Atrazine Desethyl	800	400	200	80	40	16	8	4	20	320
Azinphos Methyl	800	400	200	80	40	16	8	4	20	320
Bromacil	400	200	100	40	20	8	4	2	40	160
Butylate	200	100	50	20	10	4	2	1	20	80
Chlorpyrifos Ethyl	200	100	50	20	10	4	2	1	20	80
Chlorpyrifos Methyl	200	100	50	20	10	4	2	1	20	80
Cyanazine	200	100	50	20	10	4	2	1	20	80
Demeton	700	350	175	70	35	14	7	3.5	10	280
Diazinon	100	50	25	10	5	2	1	0.5	10	40
Dimethenamid	100	50	25	10	5	2	1	0.5	10	40
Disulfoton	100	50	25	10	5	2	1	0.5	10	40
Dithiopyr	200	100	50	20	10	4	2	1	20	80

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EPTC	400	200	100	40	20	8	4	2	40	160
Ethion	200	100	50	20	10	4	2	1	20	80
Ethoprop	100	50	25	10	5	2	1	0.5	10	40
Fenamiphos	200	100	50	20	10	4	2	1	20	80
Fipronil	200	100	50	20	10	4	2	1	40	80
Fipronil Desulfinyl	200	100	50	20	10	4	2	1	*	80
Fipronil Sulfide	100	50	25	10	5	2	1	0.5	10	40
Fipronil Sulfone	100	50	25	10	5	2	1	0.5	10	40
Fonofos	50	25	12.5	5	2.5	1	0.5	0.25	5	20
Hexazinone	600	300	150	60	30	12	6	3	60	240
Malathion	200	100	50	20	10	4	2	1	20	80
Metalaxyl	400	200	100	40	20	8	4	2	40	160
Metolachlor	600	300	150	60	30	12	6	3	60	240
Methamidophos	800	400	200	80	40	16	8	4	20	320
Metribuzin	400	200	100	40	20	8	4	2	40	160
Mevinphos	200	100	50	20	10	4	2	1	20	80
Molinate	200	100	50	20	10	4	2	1	20	80
Monocrotophos	700	350	175	70	35	14	7	3.5	10	280
Norflurazon	600	300	150	60	30	12	6	3	60	240
Oxadiazon	200	100	50	20	10	4	2	1	20	80
Parathion Ethyl	100	50	25	10	5	2	1	0.5	10	40
Parathion Methyl	100	50	25	10	5	2	1	0.5	10	40
Pendimethalin	400	200	100	40	20	8	4	2	40	160
Prodiamine	200	100	50	20	10	4	2	1	20	80
Prometon	400	200	100	40	20	8	4	2	20	160
Prometryn	400	200	100	40	20	8	4	2	40	160
Phorate	100	50	25	10	5	2	1	0.5	10	40
Simazine	200	100	50	20	10	4	2	1	20	80
Tebuconazole	600	300	150	60	30	12	6	3	60	240
Terbufos	100	50	25	10	5	2	1	0.5	10	40
Terbuthylazine	200	100	50	20	10	4	2	1	20	80
Terbufos-d10	200	100	50	20	10	4	2	1	20	100
Simazine-d10	200	100	50	20	10	4	2	1	20	100
Malathion-d7	200	100	50	20	10	4	2	1	20	100

Methamidophos, Monocrotophos are not currently analyzed in water.

- No second source standard is currently available for Fipronil Desulfinyl

Table 5B: Analyte concentrations in calibration standards and /QCS/ICV for Chlorinated pesticides (ug/L) (Test ID S-PSCL-TQ). The expected spike concentrations in LFBs/MSs are equal to L5

PEST-CL	spike	L8	L7	L6	L5	L4	L3	L2	L1	ICV/QCS
Aldrin	200	200	100	50	20	10	4	2	1	20

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Alpha-BHC	200	200	100	50	20	10	4	2	1	20
Cis/Alpha-Chlordane	200	200	100	50	20	10	4	2	1	20
Beta-BHC	200	200	100	50	20	10	4	2	1	20
DDD-p,p'	200	200	100	50	20	10	4	2	1	20
DDE-p,p'	200	200	100	50	20	10	4	2	1	20
Delta-BHC	200	200	100	50	20	10	4	2	1	20
Dieldrin	200	200	100	50	20	10	4	2	1	20
Endosulfan I	200	200	100	50	20	10	4	2	1	20
Endosulfan II	200	200	100	50	20	10	4	2	1	20
Endosulfan Sulfate	200	200	100	50	20	10	4	2	1	20
Endrin Aldehyde	200	200	100	50	20	10	4	2	1	20
Endrin Ketone	200	200	100	50	20	10	4	2	1	20
Gamma-BHC	200	200	100	50	20	10	4	2	1	20
Trans/Gamma-Chlordane	200	200	100	50	20	10	4	2	1	20
Heptachlor	200	200	100	50	20	10	4	2	1	20
Heptachlor Epoxide	200	200	100	50	20	10	4	2	1	20
Methoxychlor	200	200	100	50	20	10	4	2	1	20
Carbophenothion	200	200	100	50	20	10	4	2	1	20
Chlorothalonil	200	200	100	50	20	10	4	2	1	20
Cypermethrin	1000	1000	500	250	100	50	20	10	5	100
Dicofol	200	200	100	50	20	10	4	2	1	20
Mirex	200	200	100	50	20	10	4	2	1	20
Permethrin	1000	1000	500	250	100	50	20	10	5	100
Trifluralin	200	200	100	50	20	10	4	2	1	20
DDT-p,p'	200	200	100	50	20	10	4	2	1	40
Endrin	200	200	100	50	20	10	4	2	1	40
TMX	200	200	100	50	20	10	4	2	1	20
DCB	200	200	100	50	20	10	4	2	1	20

Table 5C: Analyte concentrations in calibration standards and CCV ICV for PCB aroclors (ug/L). The expected spike concentrations in **LFBs/MSs are 200 ppbs. Expected concentrations in CCVs are L4**

AROCLORS	SPK	L6	L5	L4	L3	L2	L1	ICV
PCB-1016	2000	1000	750	500	250	125	40	500
PCB-1221	2000	1000	750	500	250	125	40	500
PCB-1232	2000	1000	750	500	250	125	40	500
PCB-1242	2000	1000	750	500	250	125	40	500
PCB-1248	2000	1000	750	500	250	125	40	500
PCB-1254	2000	1000	750	500	250	125	40	500
PCB-1260	2000	1000	750	500	250	125	40	500
Decachlorobiphenyl **	200	100	75	50	25	12.5	4	20

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Table 5D: Analyte concentrations in calibration standards and QCS/ICV for Chlorinated pesticides in tissue (ug/L). The expected spike concentrations in LFBs/MSs are equal to L5. CCV concentrations are equal to L5. This mix is also used to analyze for dieldrin in water (W-PSCL-TQ)

	spike	L8	L7	L6	L5	L4	L3	L2	L1	QCS
PCBCL_TQ	T-CL-TQ									ICV
Aldrin	100	200	100	50	20	10	4	2	1	20
Alpha-BHC	100	200	100	50	20	10	4	2	1	20
Cis/Alpha-Chlordane	100	200	100	50	20	10	4	2	1	20
Beta-BHC	100	200	100	50	20	10	4	2	1	20
DDD-p,p'	100	200	100	50	20	10	4	2	1	20
DDE-p,p'	100	200	100	50	20	10	4	2	1	20
Delta-BHC	100	200	100	50	20	10	4	2	1	20
Dieldrin	100	200	100	50	20	10	4	2	1	20
Endosulfan I	100	200	100	50	20	10	4	2	1	20
Endosulfan II	100	200	100	50	20	10	4	2	1	20
Endosulfan Sulfate	100	200	100	50	20	10	4	2	1	20
Endrin Aldehyde	100	200	100	50	20	10	4	2	1	20
Endrin Ketone	100	200	100	50	20	10	4	2	1	20
Gamma-BHC	100	200	100	50	20	10	4	2	1	20
Trans/Gamma-Chlordane	100	200	100	50	20	10	4	2	1	20
Heptachlor	100	200	100	50	20	10	4	2	1	20
Heptachlor Epoxide	100	200	100	50	20	10	4	2	1	20
Methoxychlor	100	200	100	50	20	10	4	2	1	20
Hexachlorobenzene	100	200	100	50	20	10	4	2	1	20
Cis-Nonachlor	100	200	100	50	20	10	4	2	1	20
Trans-Nonachlor	100	200	100	50	20	10	4	2	1	20
DDE-o,p'	100	200	100	50	20	10	4	2	1	20
DDD-o,p'	100	200	100	50	20	10	4	2	1	20
DDT-p,p'	100	200	100	50	20	10	4	2	1	40
DDT-o,p'	100	200	100	50	20	10	4	2	1	20
Endrin	100	200	100	50	20	10	4	2	1	40
Mirex	100	200	100	50	20	10	4	2	1	20
TMX-surrogate	200	200	100	50	20	10	4	2	1	20
DCB-surrogate	200	400	200	100	40	20	8	4	2	40
PCB-8	100	200	100	50	20	10	4	2	1	20
PCB-18	100	200	100	50	20	10	4	2	1	20
PCB-28	100	200	100	50	20	10	4	2	1	20
PCB-52	100	200	100	50	20	10	4	2	1	20
PCB-44	100	200	100	50	20	10	4	2	1	20

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PCB-66	100	200	100	50	20	10	4	2	1	20
PCB-101	100	200	100	50	20	10	4	2	1	20
PCB-118	100	200	100	50	20	10	4	2	1	20
PCB-153	100	200	100	50	20	10	4	2	1	20
PCB-105	100	200	100	50	20	10	4	2	1	20
PCB-138	100	200	100	50	20	10	4	2	1	20
PCB-187	100	200	100	50	20	10	4	2	1	20
PCB-128	100	200	100	50	20	10	4	2	1	20
PCB-180	100	200	100	50	20	10	4	2	1	20
PCB-169	100	200	100	50	20	10	4	2	1	20
PCB-170	100	200	100	50	20	10	4	2	1	20
PCB-195	100	200	100	50	20	10	4	2	1	20
PCB-206	100	200	100	50	20	10	4	2	1	20
PCB-209	100	200	100	50	20	10	4	2	1	20
PCB-77	100	200	100	50	20	10	4	2	1	20
PCB-126	100	200	100	50	20	10	4	2	1	20

PCB-209 included in DCB total

TABLE 6: QC MEASUREMENTS AND ACCEPTANCE CRITERIA

QC MEASUREMENT	ACCEPTANCE CRITERION	CORRECTIVE ACTION
LFB, Matrix Spike precision	≤ 30%	Reanalyze/Re-extract/Flag
LFB/MS recoveries: W-PSNP-TQ	Separate statistical limits for LFBs and MSs; 60-130% for Dimethenamid, Fipronil Desulfinyl, Dithiopyr, Prodiamine, Oxadiazon. 30-100% for Tebuconazole	Reanalyze/Re-extract/Flag
LFB/MS recoveries: W-DIELDRIN	LFB stats for both LFBs and MSs	Reanalyze/Re-extract/Flag
LFB/MS recoveries: S-PSNP-TQ, WS-PSNP-TQ	50-150% except for: EPTC, Butylate, Molinate 30-120% Mevinphos, Disulfoton, Demeton 40-140% Methamidophos, Monocrotophos 20-100%	Reanalyze/Re-extract/Flag
LFB/MS recoveries: S-PSCL-TQ, WS-PSCL-TQ	Separate statistical limits for LFBs and MSs	Reanalyze/Re-extract/Flag
LFB/MS recoveries: S-PCB-TQ, WS-PCB-TQ	Separate statistical limits for LFBs and MSs for 1016&1260 60-130% for other aroclors	Reanalyze/Re-extract/Flag
LFB/MS recoveries: T-PCBCL-TQ	Separate statistical limits for LFBs and MSs 60-130 for PCB-169	Reanalyze/Re-extract/Flag

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Surrogates: W-PSNP-TQ	Simazine-d10 71-126% Terbufos-d10 50-130%	Reanalyze/Re-extract/Flag
Surrogates: W-DIELDRIN	Tetrachloro-m-xylene 31-107% Decachlorobiphenyl 50-120%	Reanalyze/Re-extract/Flag
Surrogates: S-PSNP-TQ, WS-PSNP-TQ	Simazine-d10 69-110% Terbufos-d10 50-130%	Reanalyze/Re-extract/Flag
Surrogates: S-PSCL-TQ, S-PCB-TQ, WS-PSCL-TQ, WS-PCB-TQ	Tetrachloro-m-xylene 35-108% Decachlorobiphenyl 43-149%	Reanalyze/Re-extract/Flag
Surrogates: T-PCBCL-TQ	Tetrachloro-m-xylene 53-106% Decachlorobiphenyl 61-137%	Reanalyze/Re-extract/Flag
ICV	± 30%	Reanalyze/Flag
CCV	± 20%	Re-run and recalibrate/Flag
Linearity criterion	20% RSD; 0.995 CC	Use appropriate cal fit / Re-run/ Recalibrate
Internal Std. recovery	50-200% Except for (soils only) Hexazinone-d6 25-200% Parathion Ethyl-d10 50-250%	Reanalyze/recalibrate/flag
% cal drift	± 30% of expected value	Change fit/weighing/recalibrate/flag

Statistical recovery limits for LFB/MS and surrogates recoveries are typically based on QC Manager statistics for the last five calendar years (if available). The limits are recalculated at least annually.The results of statistical calculations are saved at FLDEP1\DEAR\LABS\LAB5\CHEMISTRY\ORGANIC\QC LIMITS STATS. The statistical recovery limits are then entered into QC Manager limits tables. 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 points is available for LFBs but not for matrix spikes then LFB statistical limits may be applicable for both categories on temporary basis.

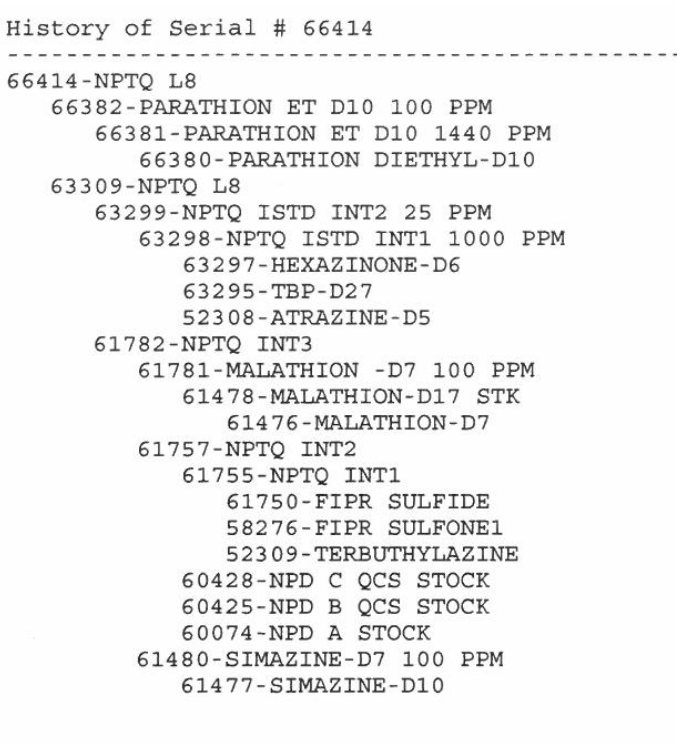
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17. APPENDICES

APPENDIX 1

Standard Preparation Procedure

Stock solutions usually come in 1mL glass vials. Take the vials out of the freezer at least 30min before preparation. Open vials and transfer the entire solution into 1mL GC vials (using Pasteur pipettes). Record the transfer date and keep the vial label.
The Intermediate Standard is prepared by diluting the Stock solution. The Working Level Standards are prepared by diluting the Intermediate Standard.
All standard preparations are recorded in the Standard/Reagent Preparation Tracker. In order to prepare fresh standards go to LIMS-Technical-Standard/Reagent Preparation Tracker. Select GC from the pull down list. Hit "Reports" and then "History". When prompted enter the standard tracking number for the standard you are going to replace. Examine the "History Tree". An example of a "History Tree" is shown below:



```
History of Serial # 66414
-------------------------------------------
66414-NPTQ L8
   66382-PARATHION ET D10 100 PPM
      66381-PARATHION ET D10 1440 PPM
         66380-PARATHION DIETHYL-D10
   63309-NPTQ L8
      63299-NPTQ ISTD INT2 25 PPM
         63298-NPTQ ISTD INT1 1000 PPM
            63297-HEXAZINONE-D6
            63295-TBP-D27
            52308-ATRAZINE-D5
      61782-NPTQ INT3
         61781-MALATHION -D7 100 PPM
            61478-MALATHION-D17 STK
               61476-MALATHION-D7
         61757-NPTQ INT2
            61755-NPTQ INT1
               61750-FIPR SULFIDE
               58276-FIPR SULFONE1
               52309-TERBUTHYLAZINE
            60428-NPD C QCS STOCK
            60425-NPD B QCS STOCK
            60074-NPD A STOCK
         61480-SIMAZINE-D7 100 PPM
            61477-SIMAZINE-D10
```

In order to get exact information on how the standard was prepared look at "history data sheets" that will show exact information on standards preparations.

Before preparing new standards consult with the GC group supervisor whether any changes to standards preparation procedures should be made. Those may include different prepared volumes, concentrations, new, additional concentration levels, etc.
All freshly prepared standards need to be entered in the Standard Preparation Tracker.

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APPENDIX 2

ANALYTE PROTECTANTS

Follow the instructions in appendix 1 to re-prepare analytes protectants solutions.

Notes: Neat D-sorbitol is hydroscopic and should be stored in a dessicator. D-Sorbitol and, especially, gulonolactone are difficult to dissolve in MeOH. To achieve complete dissolution of these components, 1 – 3 hours of hot sonication and repeated vigourous shaking (vortexing) may be needed. To avoid extensive sonication, required quantities of analyte protectants may be initially dissolved in 5 mL of water. The resulting solution may then be brought up to the final volume of 100 mL by adding methanol.The resulting solution is saturated with gulonolactone and therefore should be kept at room temperature to avoid excessive precipitation. Some precipitation, however, appears to be unavoidable. AP solution used for GC/MS 5977 analysis is a two times diluted version of a standard used for GC/MS triple quad analyses.

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APPENDIX 3

Tune check criteria

Triple Quadrupole GC/MS System Verification - Tune

Instrument Name	GC_TQ-2 / US12166802	**MS Model**	7000C
Tune Date & Time	4/24/2015 9:50:03 AM	**Source**	EI Extractor
Tune File	D:\MassHunter\GCMS\1\7000\atunes.eiex.tune.xml		

Instrument Actuals

Ionization mode	EI+	Rough Vacuum	1.36E+2 mTorr
Source Temperature	300 °C	High Vacuum	7.73E-5 Torr
Quad. 1 Temperature	150 °C	Turbo Speed	100.0 %
Quad. 2 Temperature	150 °C	Turbo Power	37.304 W
Emission Current	35.0 µA		

MS1 Checktune Results	Value	Limit	Result
Low mass assignment (target 69.00, actual 69.00)	0.00	<= 0.20	OK
Mid mass assignment (target 264.00, actual 264.00)	0.00	<= 0.20	OK
High mass assignment (target 502.00, actual 502.00)	0.00	<= 0.20	OK
Low mass isotope position (target 70.00, actual 70.10)	0.10	<= 0.20	OK
Mid mass isotope position (target 265.00, actual 265.00)	0.00	<= 0.20	OK
High mass isotope position (target 503.00, actual 503.02)	0.02	<= 0.20	OK
Low mass isotope ratio	1.06%	>= 0.5% and <= 1.6%	OK
Mid mass isotope ratio	5.68%	>= 4.2% and <= 6.9%	OK
High mass isotope ratio	9.70%	>= 7.9% and <= 12.3%	OK
Ratio of mid mass to low mass	31.75%	>= 5.0%	OK
Ratio of high mass to low mass	5.18%	>= 0.8%	OK
Low mass precursor ratio	0.13%	<= 3.00%	OK
Mid mass precursor ratio	0.05%	<= 6.00%	OK
High mass precursor ratio	0.03%	<= 12.00%	OK

MS2 Checktune Results			
Low mass assignment (target 69.00, actual 69.00)	0.00	<= 0.20	OK
Mid mass assignment (target 264.00, actual 264.00)	0.00	<= 0.20	OK
High mass assignment (target 502.00, actual 502.00)	0.00	<= 0.20	OK
Low mass isotope position (target 70.00, actual 70.00)	0.00	<= 0.20	OK
Mid mass isotope position (target 265.00, actual 265.10)	0.10	<= 0.20	OK
High mass isotope position (target 503.00, actual 503.05)	0.05	<= 0.20	OK
Low mass isotope ratio	1.12%	>= 0.5% and <= 1.6%	OK
Mid mass isotope ratio	5.58%	>= 4.2% and <= 6.9%	OK
High mass isotope ratio	9.23%	>= 7.9% and <= 12.3%	OK
Low mass precursor ratio	0.45%	<= 3.00%	OK
Mid mass precursor ratio	0.00%	<= 6.00%	OK
High mass precursor ratio	0.05%	<= 12.00%	OK

Detector			
EMV	1687	<= 2900	OK
Maximum gain factor	681	>= 100	OK

Air and Water Check	Abundance	Relative Abundance	Limit	Result
PFTBA (69.00)	14988265			
Water	72765	0.49%	<= 20.00%	OK
Oxygen	132571	0.88%	<= 2.50%	OK
Nitrogen	494093	3.30%	<= 10.00%	OK

* Nitrogen values are calculated from oxygen abundance

Agilent Technologies Page 1 of 1 4/24/2015 9:55:03 AM

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APPENDIX 4

PCB Aroclors patterns and analytical peaks

Sample EIC MRM chromatograms mean Extracted ion chromatograms for all ions used in Aroclor quantitation.

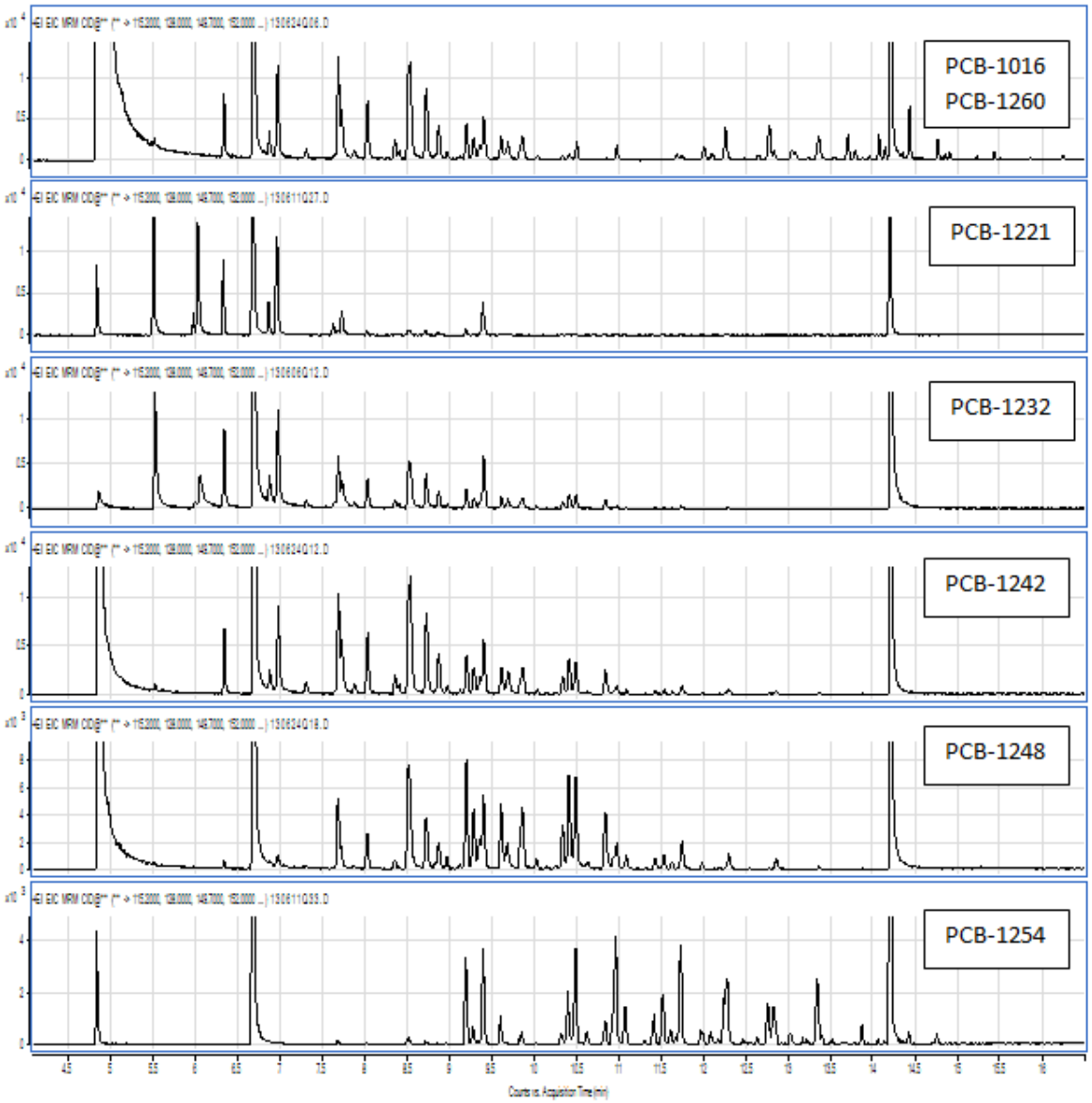


Figure 1 Sample EIC MRM chromatograms for PCB-1016, 1260, 1221 , 1232, 1242, 1248, and 1254 L3: comparison of peak patterns

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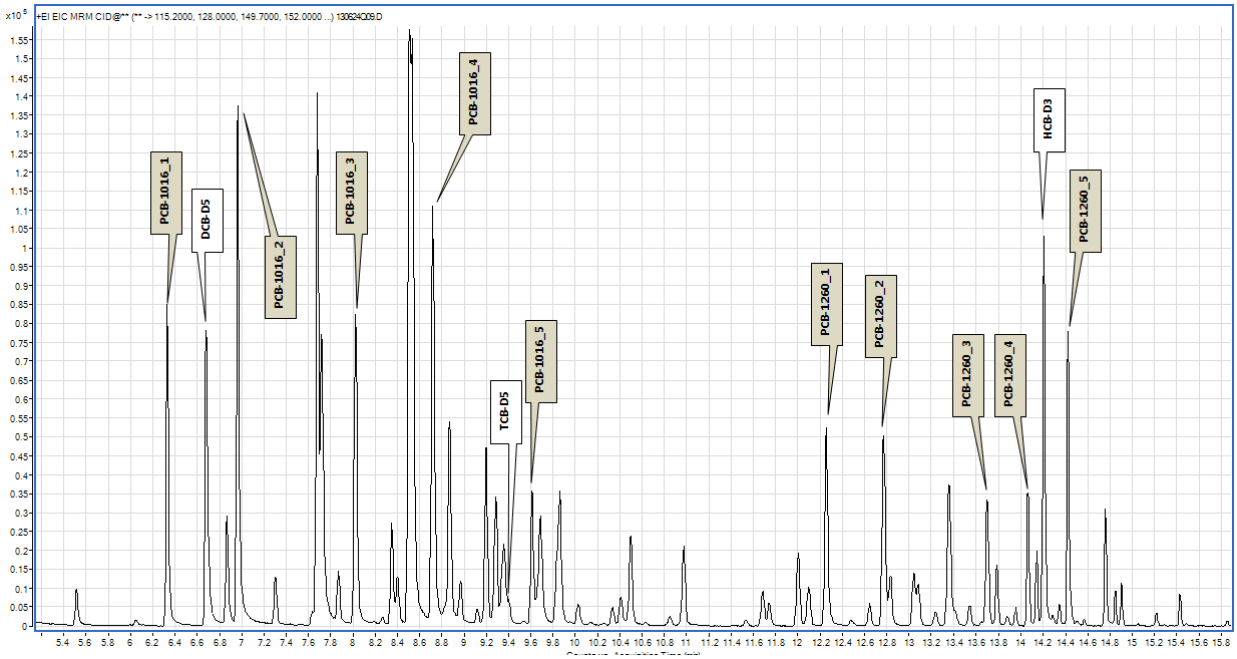


Figure 2 A sample EIC MRM chromatogram for PCB-1016 and PCB 1260 L6: Internal standards and peaks used for quantitation

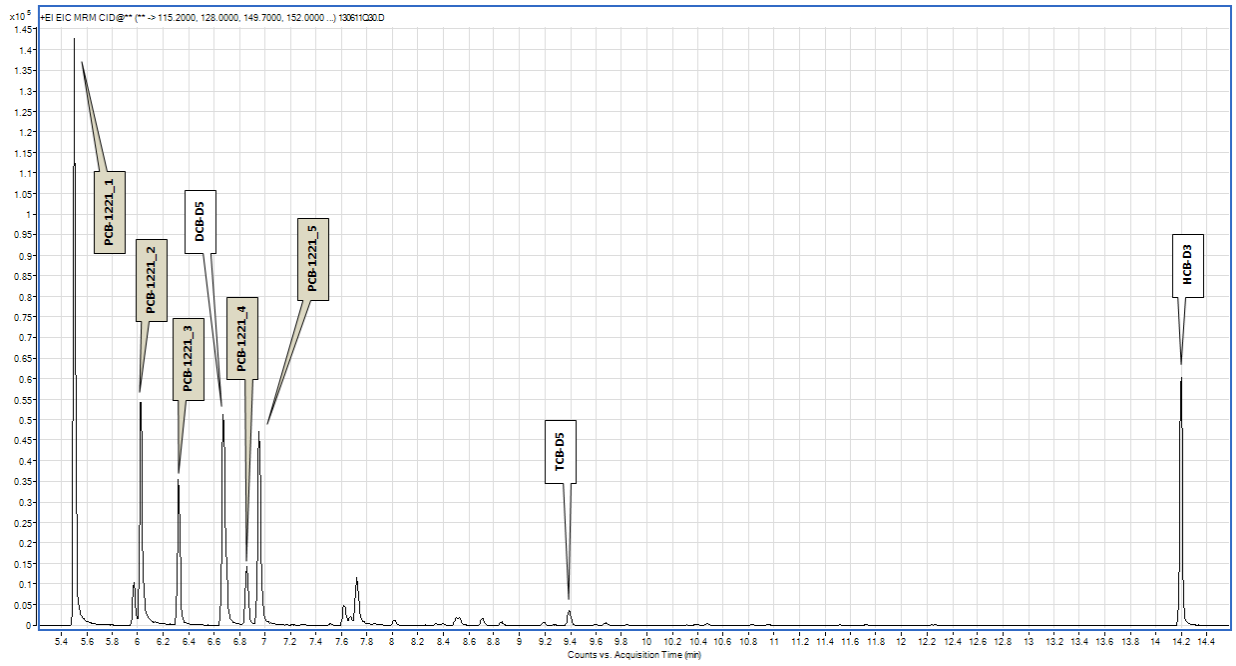


Figure 3 A sample EIC MRM chromatogram for PCB-232 L6: Internal standards and peaks used for quantitation

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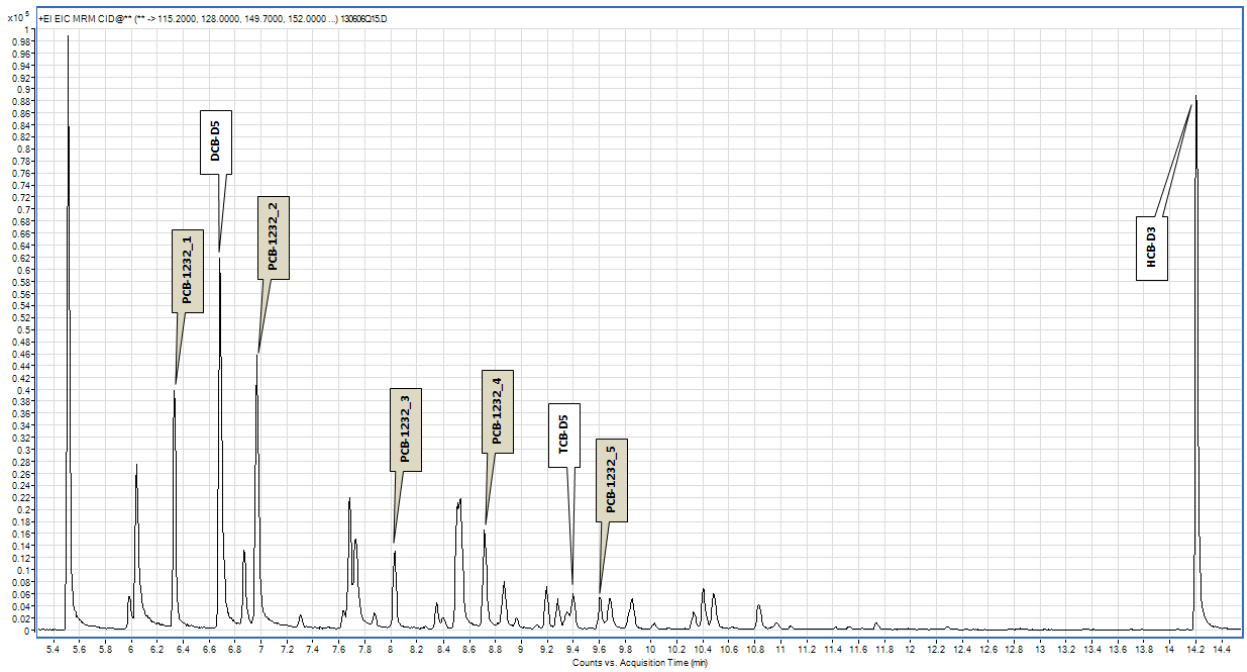


Figure 4 A sample EIC MRM chromatogram for PCB-1232 L6: Internal standards and peaks used for quantitation

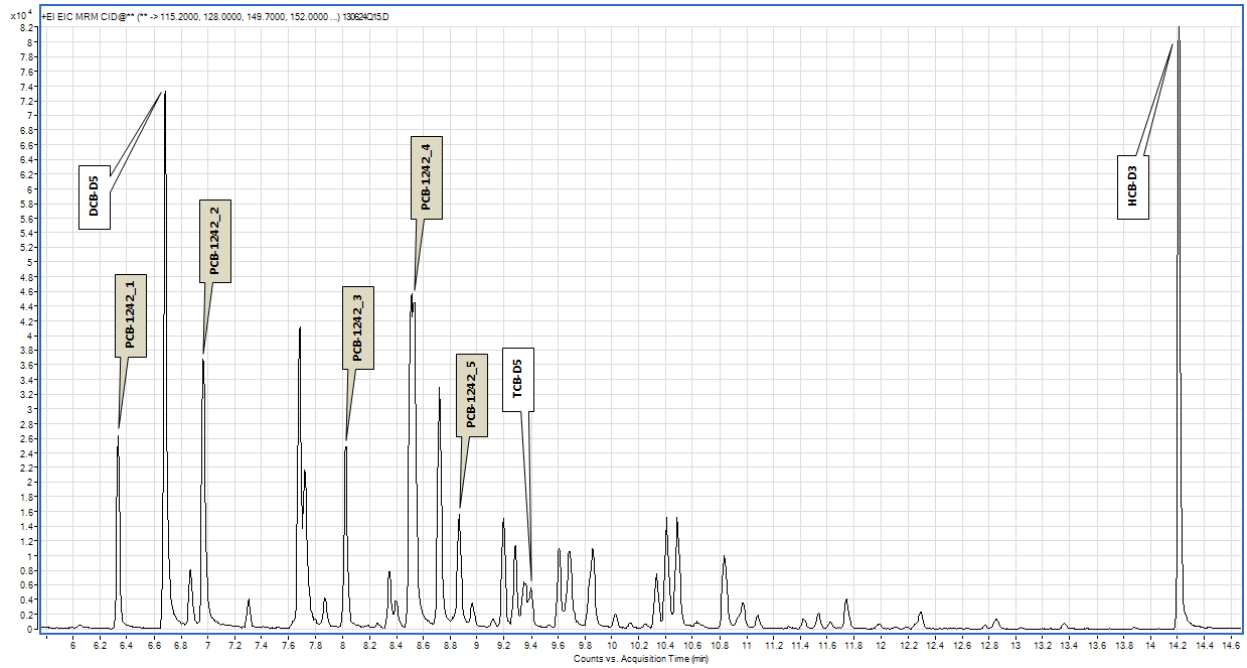


Figure 5 A sample EIC MRM chromatogram for PCB-1242 L6: Internal standards and peaks used for quantitation

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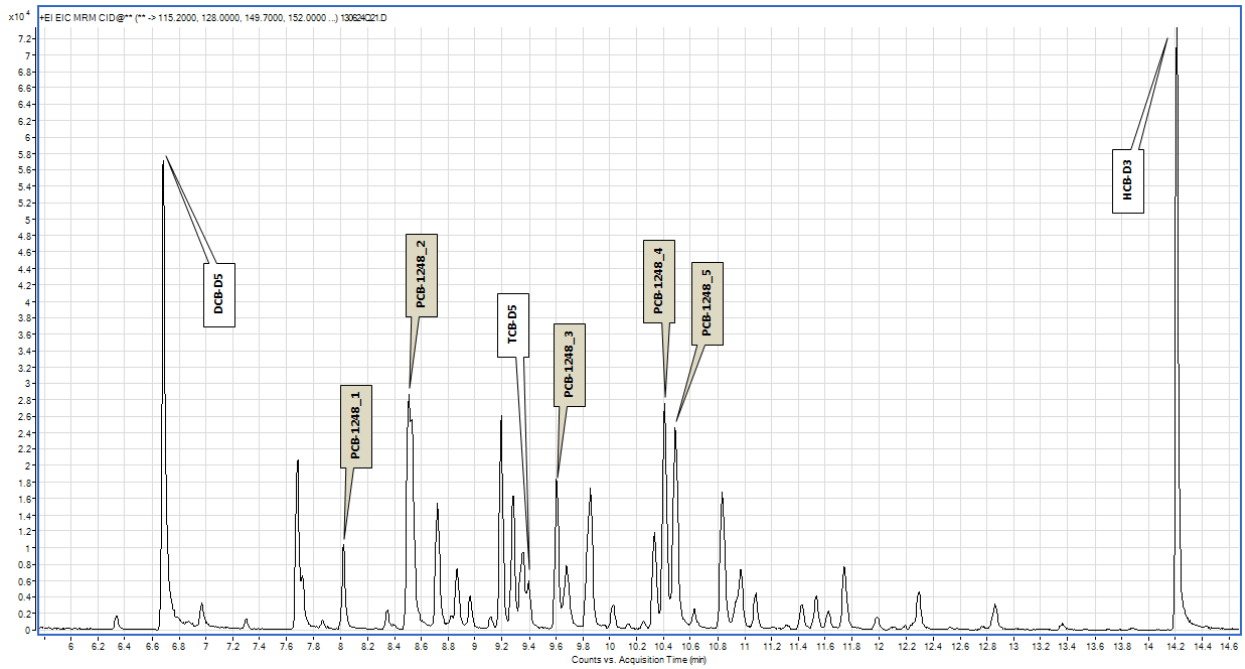


Figure 6 A sample EIC MRM chromatogram for PCB-1248 L6: Internal standards and peaks used for quantitation

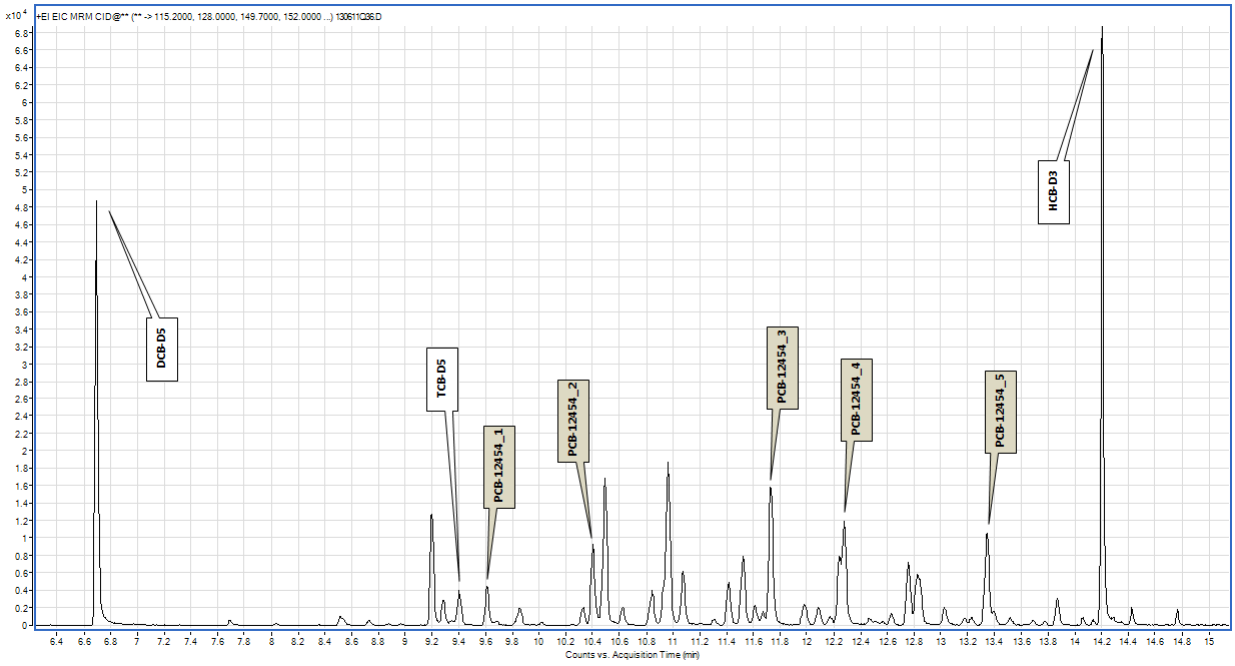


Figure 7 A sample EIC MRM chromatogram for PCB-1254 L6: Internal standards and peaks used for quantitation

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APPENDIX 5

PCB Aroclors pattern analysis in MassHunter Qualitative Analysis software

In order to accomplish PCB aroclors patterns identification, sample chromatograms are compared to the chromatograms of standards of all analyzed aroclors. In most cases this can be achieved by preparing combined extracted ion chromatograms (EIC MRM) for all MRM transitions used in aroclor quantitation. These MRM transitions are listed in the Table 4C-2 and do not include transitions for surrogates and internal standards. Sample chromatograms of this type for all analyzed aroclors can be found in Appendix 4. A Masshunter Qual method *PCB_screening_no_ISTDs.m* containing definition for these chromatograms is available for quick analysis. In complicated cases, EICs for other individual MRM transitions can also be used.

Samples containing PCB-1016 or PCB-1242, especially if weathered or at low concentration, may be challenging to identify due to similarity of corresponding aroclor patterns (Figure 1). For such cases an EIC for a single MRM transition 325.9 – 255.9 (Qual method PCB_screening_no_ISTDs_1060vs1242.m) can be used. This transition allows to focus on small peaks that are present at the later part of the PCB-1242 pattern, but are largely absent in the PCB-1016 (Figure 2).

In some cases, such as when a sample is severly weathered or may have more than one aroclor present, a definitive pattern identification may not be possible. The sample then can be quantified as the closest matching aroclor and the results reported with an appropriate comment and a qualifier (?).

APPENDIX 6

Transferring acquisition methods between TQ-1, TQ-2 and TQ-3

There are two hardware configuration variations between the three instruments that need to be reflected in acquisition methods. First, in TQ-1 and TQ-3 the pressure at the union of the front and back columns is controlled by EPC 4, while in TQ-2 this is done by EPC-6. Second, the back inlet in the TQ-1 is covered and has pressure of 1 psi, while the back inlet in TQ-2 and TQ-3 is uncovered and has pressure 0 psi. In addition, TQ-3 has a high sensitivity source that requires a different tune file and lower gain settings than ion extractor sources used in TQ-1 and TQ-2. Therefore the following steps can help to convert a method from one instrument to another.

1. Transfer and rename method.

2. Load method in the acquisition software and open GC method window.

3. Configuration –> Columns:

   First column should have the correct EPC (EPC 4 for TQ-1 / TQ-3 and EPC 6 for TQ-2) as the Outlet and the second column should have the same EPC as inlet.
4. Configuration –> Modules:

   Select He gas for the correct EPC (EPC 4 for TQ-1 / TQ-3 and EPC 6 for TQ-2) and set the other EPCs to N_2.
5. Columns: check or uncheck Control Mode as follows:

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a. Column 2 – On

b. Back inlet – Off

c. Aux EPC-6 – Off for TQ-1 / TQ-3 or Aux EPC-4 – Off for TQ-2

d. He Backflash EPC (for TQ-3) should stay Off

6. Inlets: Back Inlet Pressure box should be checked for TQ-1; for TQ-2 / TQ-3 the pressure should be 0 and Pressure box unchecked.

7. If needed, adjust injection volume by going to ALS > Front Injector and typing in the desired volume.*

8. Apply the method and exit GC method window.

9. Open MS method window.

e. The autotune file for TQ-1 / TQ-2 should be *atunes.eiex.tune.xml*, and *atunes.eihs.tune.xml* for TQ-3.

f. Gain factor for TQ-1 / TQ-2 should be 20 times higher than for TQ-3 <u>if injections of equal volume are used</u>.

10. Check the GC keypad to get rid of all blinking "Off"s, if needed, and make sure that:

a. For TQ-3 Aux EPC > Collision gas cell > Back Flash Pressure should be Off

b. EPC in use should be On (EPC 4 for TQ-1 /TQ-3 and EPC 6 for TQ-2)

c. EPC not in use should be Off (EPC 6 for TQ-1 / TQ-3 and EPC 4 for TQ-2)

d. Back Inlet Temperature should be Off

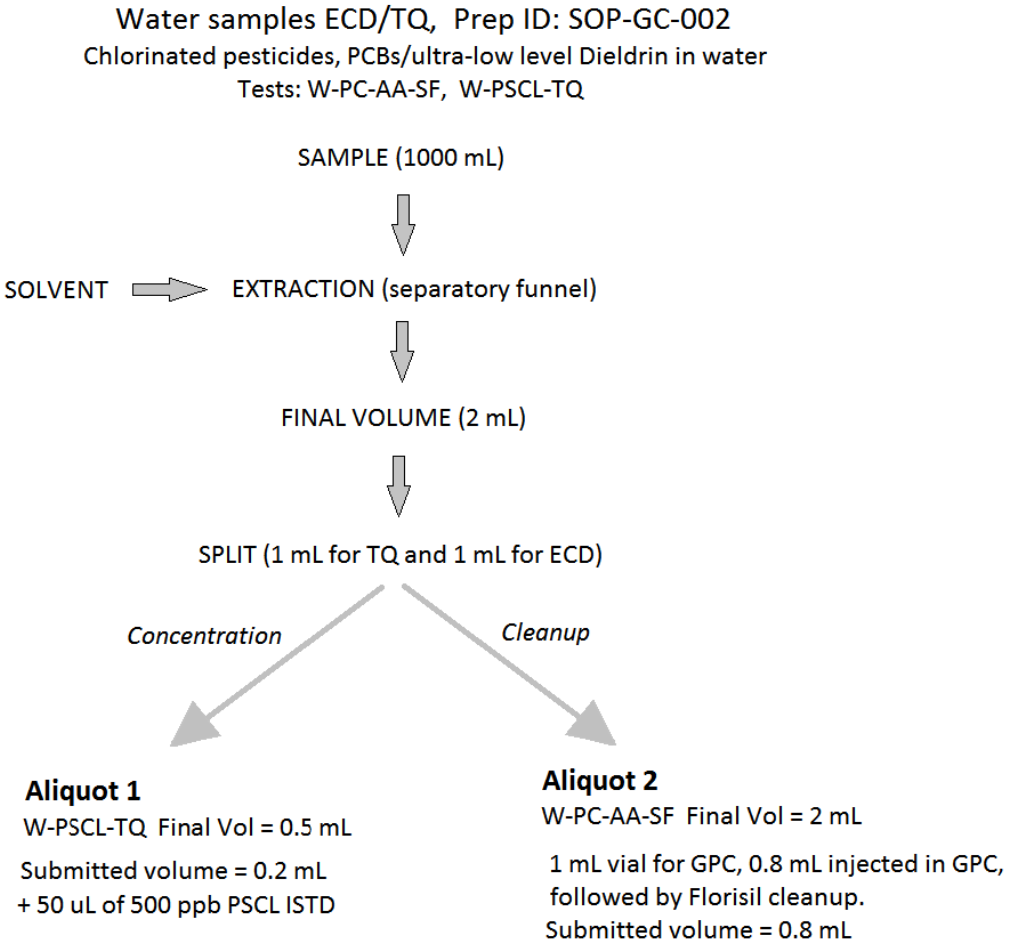
e. Back Inlet Pressure is 1 psi for TQ-1 and Off for TQ-2 /TQ-3

11. Save the method.

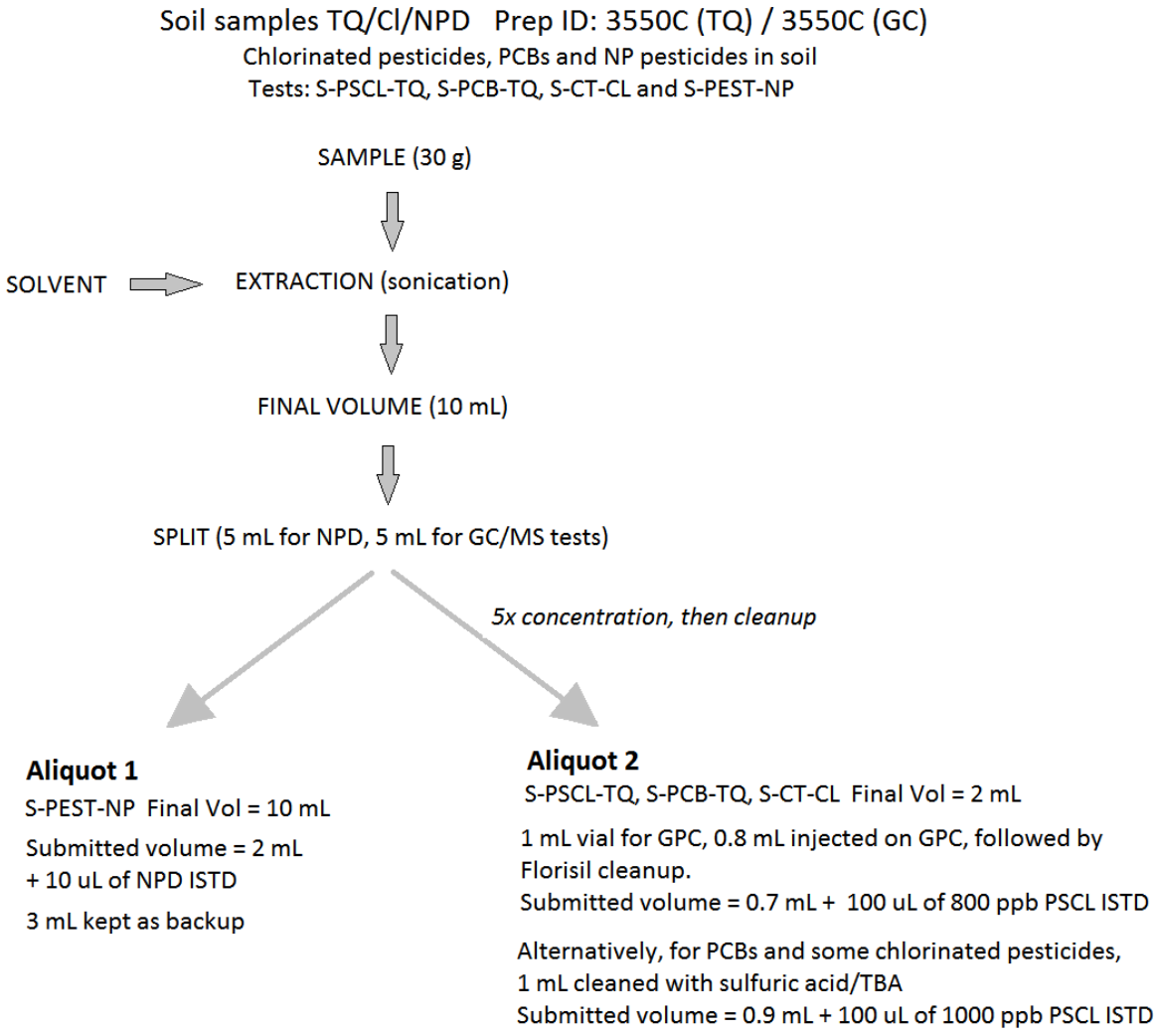
12. Try to run the method. If it does not work, repeat steps 8 and 9 as needed until the method can be used.

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APPENDIX 7: Sample Preparation Flowcharts

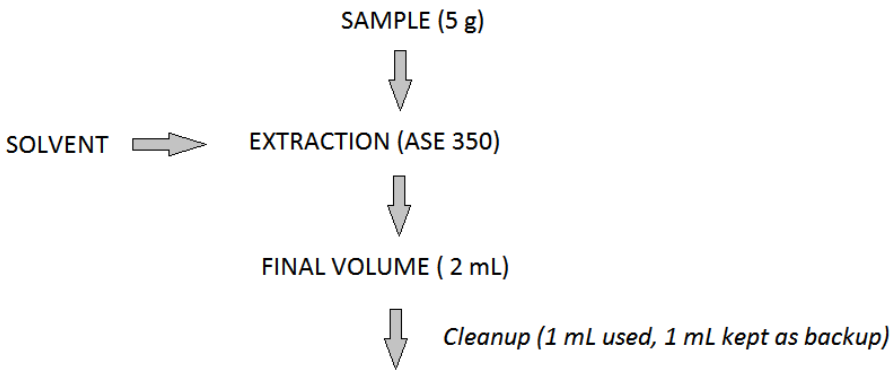


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Tissue TQ/NCl/NPD Prep ID: SOP-GC-004 (TQ) / SOP GC-004
Chlorinated pesticides, PCBs and NP pesticides in fish tissue
Tests: T-PCBCL-TQ, T-CT-CL, T-PEST-NP



1 mL vial for GPC, 0.8 mL injected on GPC followed by Florisil cleanup.
Two fractions collected.

FR1: Submitted vol = 0.7 mL + 100 uL of 800 ppb PSCL ISTD + 4 uL of NPD ISTD

FR2: Submitted vol = 0.8 mL + 4 uL of NPD ISTD (NP analytes only)

Alternatively, for PCBs and some chlorinated pesticides,
1 mL is cleaned with sulfuric acid/TBA
Submitted vol = 0.9 mL + 100 uL of 1000 ppb PSCL ISTD

Appendix 8: GC group custom report templates

GC group custom report templates for Agilent MassHunter

Agilent MassHunter Quant and Qual software reporting is accomplished through use of templates. Templates contain information on what data is drawn from a Quant batch or a Qual analysis results and how it is arranged and formatted on a page. Reports are generated in Microsoft Excel. MassHunter software comes with a selection of standard templates that are located under Computer\Data (D:)\MassHunter\Report Templates. MassHunter templates are customizable. They can be viewed and modified in MS Excel. Agilent MassHunter Workstation Software Reporting Familiarization Guide can be found in the MassHunter software distribution package. GC Group custom report templates are stored at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Organic\GCGROUP\MS-QQQ_backup_files\Templates and also in each instrument computer that uses them (typically in a custom folder within Computer\Data (D:)\MassHunter\Report Templates). Some of the GC group reports also require additional post-processing. Post-processing is automated by means of custom VBA macros added to Excel. Macros are stored in \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Organic\GCGROUP\MS-QQQ_backup_files\GC_group_custom_macros.xlam.

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Introduction to Reference Tables and VLOOKUP function

Reference tables. In order to calculate ICV, CCV, and Spike recoveries and to assign the pass/fail status to the results, MassHunter report templates require some information that is currently not available in Quant methods and cannot be automatically drawn from a Quant batch into a report. For example, expected ICV/CCV concentrations and QC control limits are currently not included with the MassHunter Quant methods and have to be made available to the report templates by alternative means. This is accomplished by adding a reference table to the corresponding report template (Figures 1 & 2). For ICV and CCV templates, the reference table should contain names of all analytes used in analysis and their expected concentrations. In addition, the Spike report template reference table also lists control limits. Many templates also use a reference table for instrument serial numbers associated with instrument names. It is recommended to place a reference table in a separate sheet within a template.

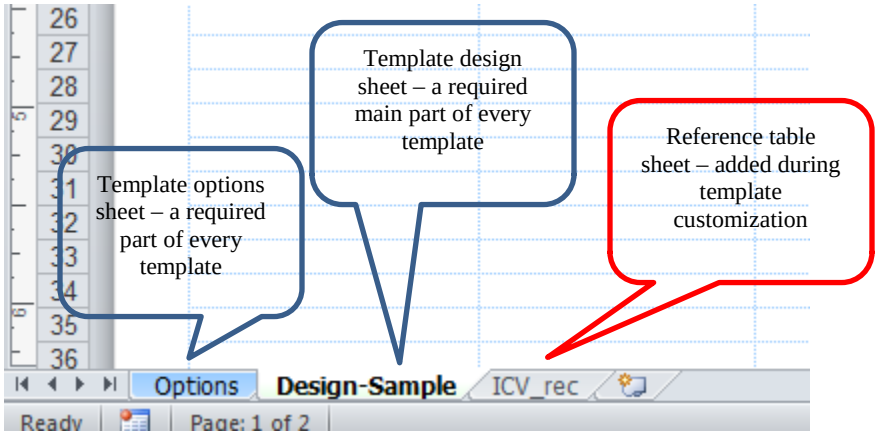
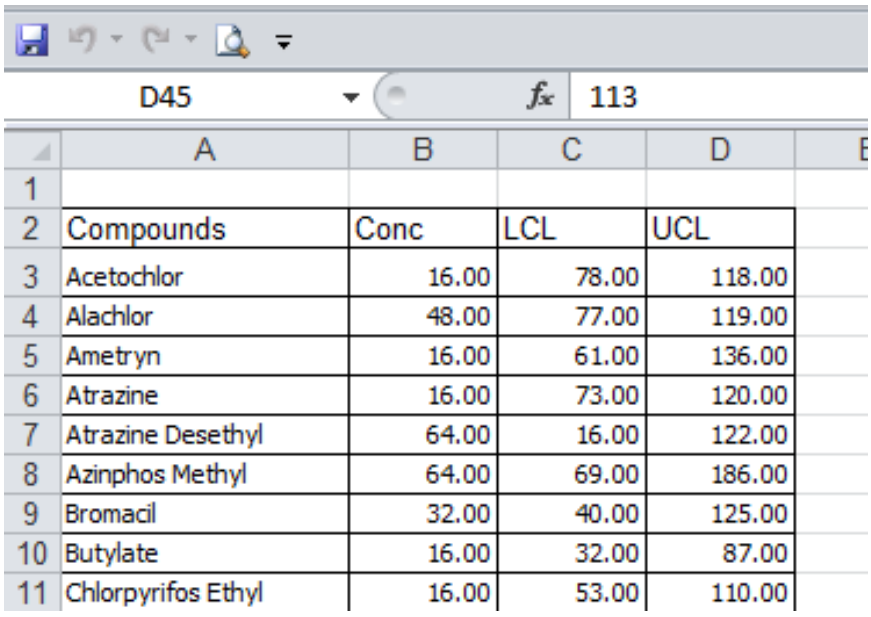


Figure 8. An example of sheets in a massHunter report template using a reference table and VLOOKUP function.



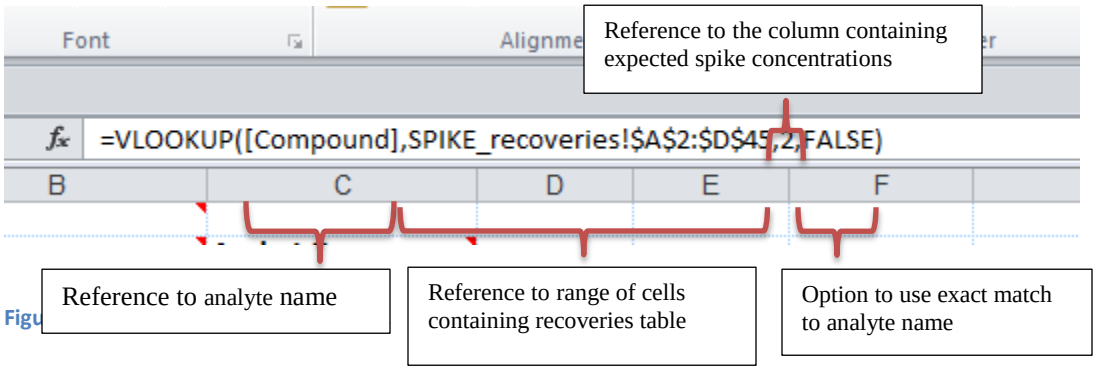
D45 | 113

	A	B	C	D
1				
2	Compounds	Conc	LCL	UCL
3	Acetochlor	16.00	78.00	118.00
4	Alachlor	48.00	77.00	119.00
5	Ametryn	16.00	61.00	136.00
6	Atrazine	16.00	73.00	120.00
7	Atrazine Desethyl	64.00	16.00	122.00
8	Azinphos Methyl	64.00	69.00	186.00
9	Bromacil	32.00	40.00	125.00
10	Butylate	16.00	32.00	87.00
11	Chlorpyrifos Ethyl	16.00	53.00	110.00

VLOOKUP function. Report templates use VLOOKUP Excel function to locate information in the reference tables. VLOOKUP function is an Excel function that finds specified information in the leftmost column of a table and returns a value found in the selected column of the same row of the table. For

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example, it can find analyte name “Butylate” in the table above and return its expected concentration. Formal representation of the VLOOKUP function is =VLOOKUP(lookup_value, table_array, col_index_num, range_lookup). For example, VLOOKUP function used for finding expected spike concentration in the Spike template reads as follows (Figure 3):



Figu

More information on use of VLOOKUP in MassHunter templates can be found in the Agilent MassHunter Workstation Software Reporting Guide.

How to change expected concentrations or control limits for existing analytes in ICV, CCV, or Spike report templates

1. To edit a template, right click on the file name and select Open. Note: if you attempt to open the file by double-clicking, a copy of the original report will open as a spread sheet instead of a template (*.xlsx instead of *.xltx).
2. In the opened template, click on the sheet that contain the reference table. Simply type in desired corrections into the table cells. **Important**: do not change analyte names (they should match exactly the names in the Quant method) and do not change number or location of rows and columns in the table (VLOOKUP looks for a specific cell range and specific columns in it).
3. When done, save the template and test it. If something did not work, a copy of the original template can be found in the backup folder at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Organic\GCGROUP\MS-QQQ_backup_files\Templates

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4. Once the modifications are tested and found satisfactory, replace the old template with the new one on each computer that uses it and in the backup folder.

How to add new analytes to ICV, CCV, or Spike reports

1. To edit a template, right click on the template file name and select Open. Note: if you attempt to open the file by double-clicking, a copy of the original report will open as a spread sheet instead of a template (*.xlsx instead of *.xltx).
2. In the opened template, click on the sheet that contains the reference table.
3. Click on the bottom right corner of the table and note the address of the cell (see Figure 4 for an example).
4. Select a row **within** the table by right-clicking on the corresponding row number on the left border of the spread sheet. Select Insert in the menu that appears. An empty row should appear above the row originally selected.
5. Type in information for the new analyte. Take care to use correct spelling for the analyte name and type in concentration and control limits into correct columns. **Important**: do not modify number or location of the columns in the table.
6. Insert and fill out more analyte rows if necessary.
7. As before, click on the bottom right corner of the table and note the address of the cell. It should have the same column as before, but a higher row number according to how many rows were inserted. E.g. after inserting two rows B8 will become B10.
8. Save changes.
9. Click on the Design-Sample sheet tab. Locate table named Results. Among the table headers, find Exp Conc header in the Results table and click on the cell directly below. This cell should contain the VLOOKUP formula for finding expected concentration (Figure 5). Check that the range of cells VLOOKUP uses matches the new range occupied by the reference table. For example, the function may read "=VLOOKUP([Compound, CCV_rec!$A$3:$B$8,2,FALSE)." Here the cells range reference is "CCV_rec!$A$3:$B$8", where $A$3 is the address of the top left corner of the table, and $B$8 is the address of the bottom right corner. (The dollar signs are added here to indicate that the location of the table is constant.) If the new analyte rows were inserted correctly, the VLOOKUP formula should have automatically changed to reflect the expanded range of the table. For example, after inserting two new rows in the table, the reference range

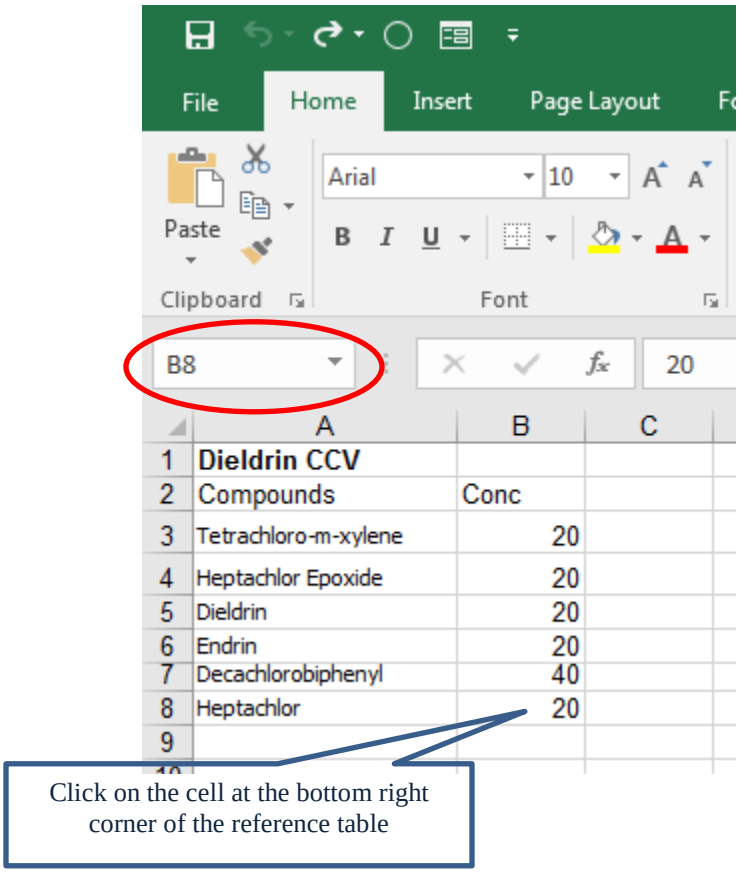


Figure 11. Checking the range of the reference table: the range of cells occupied by the data in the table can be defined as the addresses of its top left and bottom right corner. In this case they are A3 (cell with the "Tetrachloro-m-xylene") and B8.

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"CCV_rec!$A$3:$B$8" should change to "CCV_rec!$A$3:$B$10". Please note, that only the bottom right corner address should change.

10. If the analyte rows were added instead of inserted, the VLOOKUP formula would not change automatically and has to be corrected manually. To do so, click into the formula in the correct location and type in the correction. Be extremely careful not to change anything else in the formula: the extent of the correction should be replacement of one number with another (e.g. replace "8" with "10"). Do not remove dollar signs or add spaces. After the correction is complete, hit Enter to exit the formula editor and save the file.
11. Spike report templates use reference table not only for expected concentration data, but also for high and low recovery limits. For these templates, step 9 should be executed three times: for Exp Conc column, for "Limit low" and "Limit high" columns.
12. Test the template by generating a new report. If something did not work, check that the reference table is correct (especially analyte name spellings) or edit the VLOOKUP formula in its entirety (instructions on use of VLOOKUP function can be found in the MassHunter Workstation Software Reporting Guide). Note: it is possible to test the template from within the Excel, without using the MassHunter Quant. This is explained in the Reporting Guide.
13. Once the modifications are tested and found satisfactory, replace the old template with the new one on each computer that uses it and in the \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Organic\GCGROUP\MS-QQQ_backup_files\Templates.

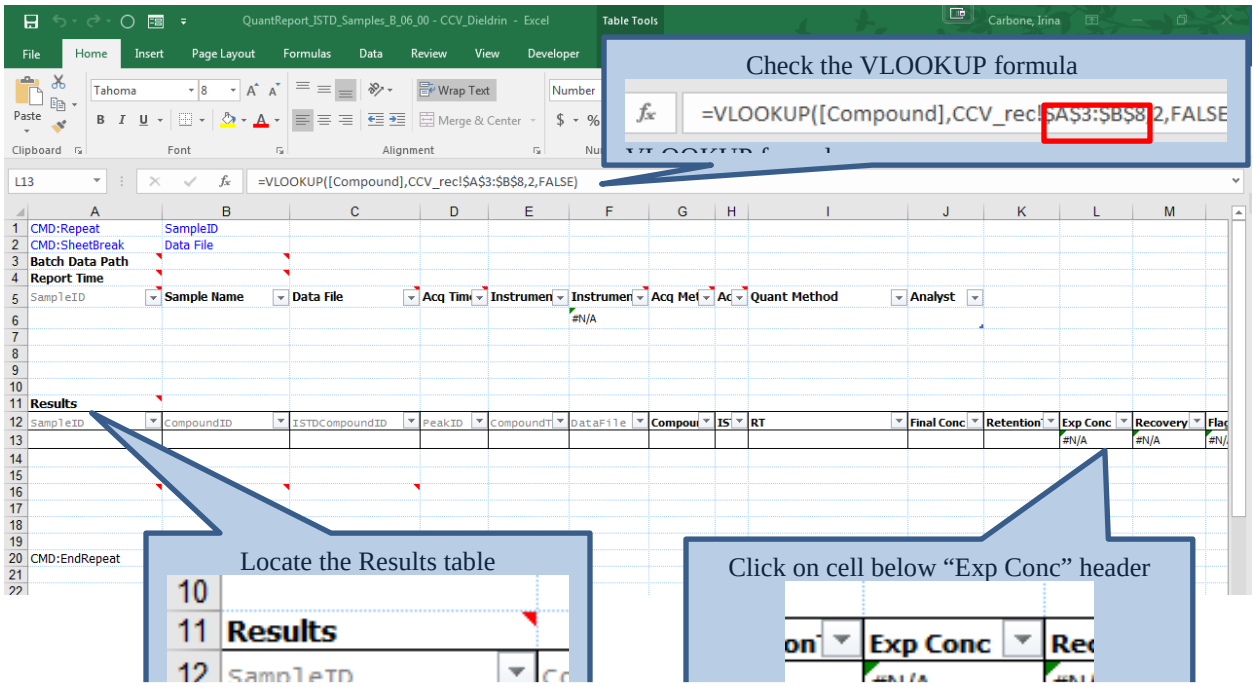


Figure 5. Viewing VLOOKUP formula for expected concentration in the Design-Sample sheet of a template

Displaying instruments serial numbers in the reports

Just like CCV/ICV/Spike expected concentrations or control limits, Instruments serial numbers are not stored in the Quant methods and have to be added to the templates by alternative means. A number of templates have an additional reference table with instrument names and their corresponding serial numbers. Instrument name is stored in the MassHunter configuration module and is available to MassHunter Quant. (To view the instrument name within Quant software, simply add an instrument name column to the results table). A template can read the instrument name from the Quant software and then use VLOOKUP function

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to get the corresponding serial number for its reference table. Serial number reference tables can be modified in the same way as the reference tables for CCV/ICV and spikes.

MassHunter reports postprocessing with macros

Several of the currently used reports require additional editing after they are generated from MassHunter templates. These are Calibration levels report, LFB and MS reports, and Decomposition Check report. Additionally, there is a printout macro for printing multi-sheet reports. All macros are written in the file named GC_group_custom_macros.xlam. A copy of this file is stored at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\Organic\GCGROUP\MS-QQQ_backup_files. Each instrument computer also has a copy. The location of the copy on instrument computers is dependent on the Window version installed. For Window 7 this location is Computer\PROGRAMS (C:)\Users\lab_gcuser\AppData\Roaming\Microsoft\AddIns\. When an *.xlam file is in this directory, Excel can read and use macros stored in it. Note: excel should be configured for macros use (Trust Center Settings > Macro Settings > enable all macros; GC_group macros are not digitally signed). To add/remove a macro in the excel ribbon, open a blank Excel file, right-click on the ribbon, select Customize the Ribbon, and choose among Macros available to add it to the desired Tab/Group.

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Appendix of Significant Changes

07/18/2013	Major expansion of the SOP due to the addition of the chlorinated pesticides and PCBs in soil tests. Changes throughout the entire SOP, including tables and standard preparation procedures.
11/25/2013	Tune procedure section was modified to explain modification to EPA 8270D DFTPP tune' CCV criterion was changed to +- 20% to follow exactly the EPA method requirement. Statistical formula to calculate surrogate recoveries was corrected. Chapter 9.6.10 was added describing quantitation of positives in detail Addition of waste tests (tables 1B and 1 C) Addition of Fipronil metabolites Sulfide and Sulfone to test W-PSNP-TQ Addition of analysis of chlorinated pesticides and PCb congeners in Tissue T-PCBCL-TQ
01/22/2014	Updated acceptance criteria in Table 6. Updated MDLs for Mirex Updated standards concentrations Changed the degradation/tailing factor check to the MRM mode.
03/03/2014	Adddition of analysis of Dieldrin in water (test ID: W-PSCL-TQ)
04/28/2014	Description of DDT decomposition /pentachlorophenol tailing factor check updated. The injection technique changed to three layer sandwich.
04/28/2015	Instruments upgraded to 7000C Updated QC limits Updates to methods tables Updated concentrations tables Updated tune check report (appendix 5)
08/06/2015	Added appendix 7; "Transferring acquisition methods between TQ-1 and TQ -2" Updated QC recovery limits 5-Nitroquinoline surrogate for test W-PSNP-TQ replaced with Simazine-d10 and Malathion-d7. New analytes added to test W-PSNP-TQ and the entire list revalidated (new GC method).
10/05/2015	Two new analytes added to test W-PSNP-TQ (Parathion Ethyl and Parathion Methyl) and a new internal standard New MDLs for Pendimethalin and Norflurazon Standard preparation chapter was re-written. Standard preparations were referenced to the standard preparations tracker.
02/02/2016	Updated QC recovery limits based on the recent statistics. Changed calibration drift acceptance criterium to 70-130% based on EPA 8270D. Updated concentrations in calibration levels for test W-PSNP-TQ (Table 5A).
04/11/2016	Requirement listed in 9.3.3.1 removed (FDEP response to CERP audit item 4d) Diatomaceous earth blank added (tissues only) in 9.4.2. (FDEP response to CERP audit item 4e). Including origin in calibration curves prohibited. Ignoring origin recommended as first choice. Paragraph 9.2.1 (FDEP response to CERP audit item 4l). Section 9.6.7 Clarification of recovery limits calculations for LFBs and Matrix spikes (FDEP response to CERP audit, section 6b)

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Addition of W-DIELDRIN test throughout the SOP.

9/15/2016 Chapter 8.1 rewritten for clarity as per CERP audit recommendation.
QC recovery limits table updated. (Table 6)
Preparation flowcharts added as appendix 6

01/17/2017 Updated QC control limits,
Appendix 5 added (PCB aroclors analysis)
Appendix 5 updated to include GC-TQ-3 (Agilent 7010 GC/MS/MS) and renamed as Appendix 6; Appendix 6 renamed as appendix 7
Updated standard concentration tables
Added PCB-169 analysis to tissue tests.

05/19/2017 Updated concentrations for analyte protectants
Updated QC control limits
Added analysis of NP pesticides in soil (S-PSNP-TQ, WS-PSNP-TQ); updates to tables 1a and 4A.

01/29/2018. Removed W-PSCl-TQ test. Added chapter about the use of PCB-1268 to determine the presence of Decachlorobiphenyl surrogate in the sample. Updated MDLs and QC limits. Appendix 8: custom report templates added. Appendix 6 updated. Added Terbufos-d10 surrogate for W-PSNP-TQ. Added new internal standards to chlorinated pesticides analysis.

9/25/2018 Brief discussion of analyzing mixes of PCB-aroclors is added. Terbufos -d10 replaces Malathion-d7 as a surrogate for S-PSNP-TQ. Added 6-new analytes to table “1A-Water”, Table 4A and Table 6. Updated table 4B. Removal of calibration points discussed (chapter 9.2.1).

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