Standard Operation Procedure for:

ANALYSIS OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS (PCBS) IN WATER BY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION (GC/ECD).

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of 31 organochlorine pesticides, and 7 aroclors (PCBs) in water as listed in Table 3. Method Detection Limits and Practical Quantitation Limits yielded by this method are also provided in Table 3.

1.2 This method is in compliance with the requirements of EPA Method 608, 608.2, 617 and Method 8081B for the parameters denoted as such in Table 5.1 of the laboratory's Quality Manual. EPA Methods 608, 608.2, and 617 are approved test procedures of the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) and Methods 8081B are listed in the SW-846 publication under Subtitle C of the Resource Conservation and Recovery Act (RCRA). Furthermore, the NPDES and RCRA compliant tests employed by the laboratory using these methods are listed below.

Laboratory Test	Test Description
W-PC-AA-SF	EPA Method 608, 608.2, 617, analysis, water samples, CWA (NPDES) compliant
TCLP-PS-CL	EPA Method 8081B analysis, TCLP samples, RCRA compliant
SPLP-PS-CL	EPA Method 8081B analysis, SPLP samples, RCRA compliant

The acceptance limits, as provided in EPA Methods 608, 608.2, 617and EPA Methods 8081B, are programmed into the Target processing software and Laboratory's Information Management Systems (LIMS) and applied automatically as part of the data processing, review, and reporting procedures. Table 5 specifies the different QC performance criteria employed for CWA (NPDES) and RCRA samples.

1.3 Performance criteria for individual analytes, based on the specific EPA method, are summarized in appendix 2 Table C. For parameters not listed in any of the EPA 600 methods mentioned above the performance criteria are based on this SOP. For parameters not mentioned in any of the EPA 8000 series methods mentioned above (ref. 15.2 and 15.3) the performance criteria are based on EPA 8000C (ref. 15.1), and/or this SOP.

1.4 Compound identification is supported by a dissimilar gas-chromatography column analysis.

1.5 This Standard Operation Procedure is restricted to use by an analyst experienced in the use of a Gas Chromatograph, in the interpretation of Gas Chromatograms, 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
- Ability to perform basic laboratory mathematics
- Knowledge of EZChrom Elite software, Target software, and FDEP Laboratory Information Management System (LIMS) software

2. SUMMARY OF THE METHOD

2.1 Water samples are extracted using the appropriate procedures listed in the Preparation SOP. The extract is analyzed using a Gas Chromatograph (GC) equipped with two capillary GC columns and two Electron Capture Detectors (ECDs) to provide confirmatory analyses for all positive hits.

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3. INTERFERENCES

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 method blanks as described in Section 9. 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 detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 550 °C for 8 hours. 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. See SOP GC-003-2 for more details (reference 15.12). 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. Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large late eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Matrix interferences may be caused by organic contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures described in the Prep SOP can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDLs listed in Table 3.

In case of observed interferences with the parameters of interest, there are several options the analyst can use to remove or alleviate the problem:

1. Process the sample extract with a validated cleanup procedure (see Prep SOP GC-002-2. reference 15.13)
2. Use another column type, length or diameter (if available)
3. Use another detector type (GC/MS, NPD)
4. Dilute

In case the interference cannot be removed increase the MDL to the level of the lowest value obtained in two channels.

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 and which 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,

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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 precession of the sampling process.

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

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

4.8 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.

4.9 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.

4.10 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.

4.11 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.

4.12 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 deionized water.

4.13 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).

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

where:
X1 and X2 are the two measurements

4.14 QUALITY CONTROL CHECK STANDARD (QCS): 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.

4.15 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.

4.16 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 nine (9) of this SOP. The calibration standards should be prepared using the same type of solvent as the final sample preparation solvent.

4.17 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 added to each field and QC sample prior to extraction and are used to monitor the preparation.

5. APPARATUS AND EQUIPMENT

5.1. Gas Chromatograph: Agilent Technologies HP 7890 capable of four steps temperature programming, with dual electron capture detectors, dual capillary split/splitless injectors and a dual HP 7683 Automatic Sampler. The GC and GC Automatic Sampler operating parameters are illustrated in Table 1a, b, c and Table 2 of the Appendices.

5.1.1. The first analytical column is a DB-5 (or similar), J & W fused silica capillary, 30 m x 0.32 mm x 0.25 um or similar column.

5.1.2. The second column is a DB-608 (or similar), J & W fused silica capillary, 30 m x 0.32 mm x 0.50 um or similar column.

5.2. Data system

5.2.1. A computer system is interfaced to the Chromatograph 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 ”EZChrom Elite” software from Agilent Technologies Inc., (see 15.10) for data acquisition, and Thermo Electron Corporation’s “Target” chromatography software (see 15.11) for data processing.

5.2.3. For reporting data, the system currently uses: FDEP LIMS.

5.3. Gases

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

5.3.2. Nitrogen, UPC Grade, is used as the make up gas for the ECD detectors. The N_2 is passed through an oxygen and a hydrocarbon filter before entering the GC.

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5.3.3. Gases are delivered to the instruments by Laboratory Compressed Gas Manifold System.

6. REAGENTS AND CHEMICALS

6.1. Solvents

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

6.2. Stock and Intermediate Standards

6.2.1. Individual stock standards are concentrated standards prepared from neat standards (approximately 100% purity) once a year. The concentration for individual stock standards is usually 1,000 ug/mL. Stock Standards mixtures are prepared from neat standards. Their concentrations are multiples of 1,000 ug/mL to match the ratios in the working standards. Standards may be prepared in the DEP laboratory or purchased from a certified manufacturer (ISO 9000 or EPA certified).

6.2.2. Intermediate standard solutions are mixture or individual standards used to prepare working standards. They are prepared in our lab from stock standards by mixing / diluting with iso-octane or other appropriate solvents or can be purchased from a certified manufacturer (ISO 9000 or EPA certified). There are two standard mixtures used in this procedure: ECD A, ECD B, and nine individual standards: PCB 1016, PCB 1221, PCB 1232, PCB 1242, PCB 1248, PCB 1254, PCB 1260, CHLORDANE, TOXAPHENE. PCB Aroclors 1016 and 1260 are usually mixed together to form what is referred to as PCB 1060. The concentrations of the components in the intermediate standards are listed in Table 4. Standards are replaced once per year. New standards are checked vs. a second source standard (QC Standards), after diluting them to one of the working standard levels (usually Level 3, middle level). The criterion of acceptance is typically +/- 10% difference. All standard preparations and verifications are recorded in the Standard Preparation Tracker located in FDEP LIMS. A list containing all standards with their serial numbers used in the analysis must be part of analysis documentation folder.

6.3. Working Standards (Calibration standards)

6.3.1. Working standard solutions are a series of diluted individual or mixture standards in iso-octane. They are used for calibration and are prepared by diluting intermediate standard solutions with iso-octane. Freshly prepared standards are checked vs. newly prepared Second Source Standard (QCS). The acceptance criterion is +/- 10% difference.

6.3.2. The concentrations for each analyte in the diluted standards are listed in Table 4.

6.4. Spiking Solution

6.4.1. 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.

6.4.2. Spike solutions are prepared by diluting stock or intermediate standards with acetone. These solutions are prepared from a different source then the calibration standards, usually the same source as the one used to prepare QCS standards. Concentration of the parameters in these solutions are listed in Table 4.

6.4.3. Freshly prepared spike solutions are checked vs. valid working standards. The acceptance criterion is +/-10 % difference.

6.5. Quality Control Check Standards (QCS)

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6.5.1. Quality Control Check Standards are prepared from a source (or batch), other than calibration standards, that is certified and traceable. Usually they are prepared at middle calibration level (Level 3). These standards are used to check the integrity of the calibration standards and are run and analyzed whenever an initial calibration curve is built. The acceptance criterion is +/- 15% difference.

6.6. Refer to Appendix 1 for detailed standard preparation.

6.7. For spiking policy see DEP SOP GC-001-2, paragraph 3.5 (ref. 15.15)

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1. Samples must be collected in glass containers.

7.2. All samples must be iced or refrigerated at 4 ºC or less from time of collection until extraction.

7.3. All water samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction. If 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.

7.4. All sediment and waste samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.5. All sample extracts must be refrigerated at 4 ºC or less from the time of extraction until analysis.

8. SAMPLE PREPARATION PROCEDURE

8.1. See Preparation SOP GC-002-2 “EXTRACTION OF ORGANOPHOSPHORUS, ORGANONITROGEN, ORGANOHALIDE PESTICIDES AND PCBs FROM WATER, WASTE, SEDIMENT/SOIL, PUFS AND FILTERS FOR SUBSEQUENT ANALYSIS BY GC or GC/MS TECHNIQUES.” “(reference 15.13).

9. GENERAL DESCRIPTION OF GC/ECD ANALYSIS

9.1. Pre-Run Equipment Maintenance

9.1.1. Before starting an analysis run sequence, an initial checking and maintenance of the instrument has to be performed.

9.1.2. Initial checking and maintenance of the instrument consists mainly in the following steps:
- 9.1.2.1. Check the detector signals to be in the acceptable range
- 9.1.2.2. Run and analyze an Endrin/DDT mixture standard and determine the % decomposition
- 9.1.2.3. If % decompositions exceed the accepted limit of 15% for any of these components then:
- 9.1.2.4. Clean and refill solvent vials in the autosampler turret.
- 9.1.2.5. Replace the injector liner, cut 3-5 inches of the column, replace the injector gold seal.
- 9.1.2.6. Re-determine the % decomposition and make sure that is below the accepted limit
- 9.1.2.7. Run and Instrument Blank and look for Instrument Contamination.
- 9.1.2.8. In case the instrument is contaminated raise the furnace temperature to 260 ºC and leave it overnight.
- 9.1.2.9. Re-check for Instrument contamination and if needed repeat the procedure until the instrument is contamination free.

9.1.3. Troubleshooting following runs producing poor data quality.

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If root cause analysis of runs with poor data quality indicates an instrument performance problem then more detailed troubleshooting may be needed to address the issue. The following are the steps that may need to be taken to restore the performance of an ECD instrument:

9.1.3.1. If after the second column trimming the chromatographic performance is not restored the column may need to be replaced.

9.1.3.2. Clean or replace the autosampler syringe. Surprising numbers of chromatographic problems are caused by dirty autosampler syringes.

9.1.3.3. Clean and bake the injection port.
9.1.3.4. Check inlet and detector assemblies for leaks using electronic leak detector. Fix any leaks discovered.

9.1.3.5. Replace the detector side liner and ferrule.

9.1.3.6. If excessive noise is observed in the baseline, check the gas lines for leaks and verify the purity of gases used (helium, nitrogen). Replace the gas lines filters, if needed.

9.1.3.7. If the detector signal goes over 1000 (at 325 C), consider sending the detector for cleaning or replacing the detector (at Agilent's discretion).

9.2. Summary of GC/ECD Analysis

9.2.1. The analysis of samples is accomplished by using two dissimilar fused silica capillary columns, usually a DB-5 and a DB-608 or similar column (usually 0.32mm ID/30m/0.25-0.50 um).
9.2.2. One of the two columns, based on the best performance, is chosen by the analyst to be "primary". The "primary column" is used to report the results. Important criteria for choosing the "primary" column:
9.2.2.1. Stable retention time windows during the entire run sequence
9.2.2.2. The best chromatography (no tailing or fronting, no impurity interference with surrogates of target components)
9.2.2.3. The best calibration curves especially for target positives
9.2.2.4. The best LCS/Matrix Spikes results
9.2.2.5. The smallest number of CCV failures
9.2.2.6. The best surrogates results
9.2.2.7. The lowest %decomposition for Endrin/DDT

9.2.3. Identification and quantification of positive hits.

9.2.4. Identification of positives requires all of the following quality criteria to be met:
9.2.4.1. Use of an updated single (through origin) or multi-point calibration (updated Retention Times and Response Factors).
9.2.4.2. Stable retention time windows (all calibration check standards are within the calibration windows).
9.2.4.3. Recoveries for surrogates and spikes are within the control limits.

9.2.5. All samples are analyzed in two columns for confirmation of the positives. The LFBs, Matrix Spikes and positive reported results, are based on the "primary column" (chosen by the analyst). If for some analytes QC criteria in the primary column are out of acceptable range, due to matrix interference or other problems, the results will be reported using the values found in the confirmatory column if the QC criteria are within limits.

9.2.6. A single peak target component is identified as positive if its peak is detected within its retention time window in both columns and the response exceeds the MDL. A multiple peak target

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components like Toxaphene, Chlordane, or Aroclors are identified primarily by pattern recognition. The amount of the prospective positive found in one column has to be confirmed by the amount found in the other column. Criterion for the amount confirmation is equal to or less than +/- 30% difference between the two columns values. For Toxaphene this criterion is equal to or less than +/- 50% difference. If besides retention time, there is other evidence that the target analyte is a positive, and the amount in two column does not match, the result will be reported based on the smallest value found in the two columns, and it will be qualified as estimated (J).

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9.2.7. Quantitative analysis is accomplished by the external calibration mode. The calibration fit used is linear, Average Response Factor or quadratic. For building an initial calibration curve a minimum of 5 calibration levels must be used. At least six calibration levels are required for quadratic fits. The linearity of the calibration curve is defined by an RSD of 10% or 20% of the Response Factors (see Table B), or by a Correlation Coefficient greater than 0.995. After identification, all positives are quantified. If the quantity found is not within the calibration range the samples are diluted or re-run with a multilevel calibration curve.

9.2.8. The analyst should monitor the performance of the extraction and cleanup procedures by spiking each sample, QC sample and Method Blank with pesticide surrogates. Because GC/ECD analysis is subject to interferences, two surrogates are to be used. Decachlorobiphenyl (DCB) is the primary surrogate, and should be used whenever possible. However, if recovery for DCB fails or is impossible to determine, then TMX (2,4,5,6-tetrachloro-m-xylene) should be evaluated for acceptance (See 15.1). To determine acceptance accuracy limits for surrogates the following procedure should be used (See 15.1): (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 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 coefficient for n-1 degrees of freedom (n=number of measurements).

Control Limits are checked and updated once per year. The statistical control limits can be replaced by statutory control limits if they are practically similar.

9.2.9. If, surrogate recoveries are outside control limits, the sample has to be re-run, and re-analyzed. If surrogates fail again, sample must be re-extracted and re-analyzed. If the sample exceeded the holding time for extraction, and the recovery is biased high, the re-extraction is not required and the reported positive hits have to be qualified as estimated with the following comment entered in the Sample Report: “Estimated values for “parameter” are due to surrogate recovery for TMX/DCB out of control limits”. If surrogates are missing or the recovery is biased low, samples should be re-extracted and re-analyzed even if they are beyond holding time.

9.2.10. Absolute Retention time windows are used for the identification of target analytes. The absolute retention time window is assessed during initial calibration as +/- 0.035 minute of the mean RT of the analyte.

9.2.11. Calibrations using a single level standard (through origin) CHLORDANE, TOXAPHENE, and INDIVIDUAL AROCLORS are routinely run for screening / identification purposes. A full calibration for PCB 1016+1260 is always run. If there are identified hits at the PQL level or above, the samples have to be re-run and re-analyzed using a multiple levels calibration curve...

9.2.12. The decomposition of DDT and Endrin is evaluated by injecting an Endrin/DDT decomposition standard (containing Endrin at 100 ug/L and DDT-p,p’ at 100 ug/L) at the beginning of each sequence run and at least every 12 hours afterwards. Presence of DDE, DDD, Endrin Aldehyde and

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Endrin Ketone indicates breakdown. Before starting a run sequence maintain the instrument until the breakdown is less than 15 % in both columns for both DDT and Endrin. The Endrin/DDT decomposition mix chromatograms are analyzed using "% Dec. Target sublist". Calculate the breakdown as follow:

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

"If the 12 hours interval (beyond the initial) Endrin/DDT decomposition check fails (exceeds 15%), rerun and reanalyze those samples in which DDT and /or Endrin and their decomposition products were detected. If the samples are beyond holding time, flag the results as estimated and include appropriate comments."

9.2.13. To demonstrate that interferences from the analytical system, reagents and glassware are under control, the analyst must analyze one Instrument Blank (clean Isooctane) in the beginning of each run sequence and one Method Blank (extraction blank) for each extraction batch. A blank will be within acceptable range, if the concentration in that blank of any analyte of interest is below the analyte MDL and surrogate recoveries are within acceptable limits.

9.2.14. In case a positive identification is found in the instrument blank, the instrument must be cleaned and the sample(s) rerun/reanalyzed.

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

9.3. Instrument Initial Calibration

9.3.1. Quantitation of a positive hit at PQL or higher level for all target components is accomplished by using most commonly a linear or quadratic fit of the calibration curve. To create an initial calibration curve using external standard procedure, at least five or three (see Table B) standard calibration levels should be used. Whenever quadratic fit is applied at least six calibration standards are required. One of the calibration levels must be at a concentration lower than or equal to the PQL, but higher than MDL. The other concentrations should correspond to a range of concentrations for which an acceptable linear/quadratic calibration curve can be drawn. The Chromatography Software will calculate the ratio of response to the amount injected (calibration factor).

9.3.2. The system is considered to be in initial linear calibration if the Relative Standard Deviation (%RSD) of the analyte calibration factors (using peak area calculation) is less than or equal to 10% (water-CWA projects) or 20% (water-RCRA projects) or the Correlation Coefficient is not smaller than 0.995. Linear fit is chosen as a first choice for the calibration curve fit in Target software followed by average response factor (mathematically equivalent to weighted linear) and then followed by quadratic fit. Do not use the "include origin" option for calibration fits. The calibration curve is additionally checked by re-fitting the lowest calibration point back to the model. The calculated amounts for each of the standard components should be within 20% of the expected values.

9.3.3. All initial calibration curves shall be checked vs. appropriate QCS standard. %Recovery must be within +/- 15%. If this Quality Criterion fails for parameters reported as positives, a new calibration curve must be built, samples re-run and reanalyzed. If the samples are expired, affected results must be reported as estimated.

9.4. Continuing Calibration Verification (CCV)

9.4.1. After initial calibration, the detector responses for all parameters are checked on a continuing basis, at least once for every 12 hrs by using an continuing calibration verification check standard (CCV). A CCV is also run at the end of the run sequence after all the samples are analyzed. Criterion of

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acceptance for calibration verification is +/- 10 or 15% (NPDES projects, depending on the analyte) or +/- 15 % (RCRA projects) of initial calibration. The channel with acceptable CCV checks will be used to quantify and report the positives if all other quality criteria are met. If CCV fails in both channels, all samples bracketed by this standard have to be re-run for all identified positive hits exceeding PQL level. If the samples are beyond analysis holding time, all reported positive hits with failing CCV must be flagged as estimated (J).

9.4.2. If CCVs do not meet method requirements the associated analytical results must be qualified in accordance with Lab SOP CM-008-1 (see 15.14).

9.5. Analysis Run Sequence.

9.5.1. 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:

- iso-octane blank (equipment blank)
- Endrin/DDT decomposition Check
- PCB 1221 L3
- PCB 1232 L3
- PCB 1242 L3
- PCB 1248 L3
- PCB 1254 L3
- PCB 1016/1260 Level 3
- Chlordane Level 3
- Toxaphene Level 3
- ECDA+B calibration set (Levels 1,2, 3, 4, 5,6,QCS
- PCB-1016+1260 calibration set (Levels 1,2, 3, 4, 5,6,QCS
- CCVs for all standard mixes with multipoint calibrations
- Endrin/DDT decomposition check
- Method Blank (MBLK)
- GPC Blank 1
- GPC Blank 2
- Laboratory Control Sample (LCS)
- Sample Matrix Spike (MS)
- Sample Matrix Spike Duplicate (MSD)
- Samples for up to 12 hrs
- Endrin/DDT decomposition check
- ECDA+B CCV
- PCB-1016+1260 CCV
- Samples for up to 12 hrs
- Endrin/DDT decomposition check
- ECDA+B CCV
- PCB-1`016+1260 CCV
- PCB 1221 L3 QCS
- PCB 1232 L3 QCS
- PCB 1242 L3 QCS
- PCB 1248 L3 QCS
- PCB 1254 L3 QCS
- Chlordane Level 3 QCS
- Toxaphene Level 3 QCS

Endrin/DDT decomposition checks and CCVs are run every 12 hrs.

9.6. Data Processing

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9.6.1. Identification

9.6.1.1. Analytes are identified by matching retention times with those that are in the standard chromatographs. For Toxaphene, Aroclors and Chlordane the identification is based also on pattern recognition.

9.6.2. Quantification

.

9.6.2.1. 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 Target 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 15.19). Currently, the Target Software doesn't perform calculations to determine the concentration of the analyte in the sample. This is done in QC Manager according to the following formulas::

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

  where:

- C_X -The concentration, in ug/L, of the analyte in the sample extract determined by Target.

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

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

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

9.6.2.2. Toxaphene quantification is significantly more complicated than that of single component parameters. The GC pattern of a Toxaphene residue may differ considerably from that of the calibration standard. Depending on the sample substrate and its history, Toxaphene residue may consist of any combination of constituents from Technical Toxaphene standard and products of degradation caused by exposure to environmental factors such as water or sunlight. Due to this inability to predict the GC pattern for Toxaphene, it is not possible to prescribe a single method for quantification. The analyst can chose between "Peak method" and "Total area method" depending on which is more appropriate for the sample.

9.6.2.3. In the "Peak method" approach, the analyst chooses 5-7 predominate peaks covering the whole elution range of the Toxaphene standard equally. These peaks are not supposed to co-elute with other targeted chlorinated parameters or other unidentifiable matrix peaks. This approach is to be considered whenever the GC pattern in the sample and standard are similar, or when the sample matrix or other contaminants will significantly interfere with the Toxaphene GC pattern.

9.6.2.4. In the "Total area method" approach, the analyst chooses the total area of the GC Toxaphene standard chromatogram for calibration and quantification. This method is the best choice when Toxaphene is the major contaminant, and in the case of no significant matrix interferences. This method may require subtraction of major interfering peaks.

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9.6.2.5. For Chlordane technical the "Peak method" typically uses three predominant Chlordane peaks, namely Alpha-Chlordane, Gamma-Chlordane and Trans-Nonachlor.

9.6.2.6. For PCB aroclors five peaks are normally used for quantification.

9.6.2.7. Methoxychlor usually coelutes with the second Dicofol peak (called Dicofol conf) on DB-5 column (detector B in Target software). Therefore, Metoxychlor analysis is based on DB-608 results and it may require GC/MS confirmation if a suspected positive is found. In some cases Dicofol positive hits may also need to be confirmed by GC/MS.

9.7. Reporting results in FDEP LIMS.

9.7.1. QC results, MDLs, and Positives are reported in the FDEP LIMS using the Target upload program and QC Manager (see 15.11)

9.7.2. Following data are uploaded to LIMS:

9.7.2.1. MBLK, ,LCS(LCSD), MS/MSD and CCVs Recoveries
9.7.2.2. LCS/LCSD or MS/MSD RPDs
9.7.2.3. Surrogate Recoveries for Samples and MBLK
9.7.2.4. Positives and MDLs for Samples
9.7.2.5. MDLs for Method Blank

9.7.3. Qualified Data are reported based on DEP SOP LB-027-1 (see 15.14)

10. QUALITY CONTROL

10.1. For QA/QC see the Lab SOP GC-001-2 (see 15.15).

10.2. QC criteria pertaining this SOP are summarized in Table 6.

10.3. 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, making use of the following review / authorization checklist (see also Lab SOP OG-003-2.):

- Check sample preparation report
  - procedure
  - surrogate and spiking solutions
  - preparation holding time
- Check customer special requests
- Check initial calibration for quality criteria
- Check continuing calibration verification (CCV) standards
- Check surrogate recoveries
- Check accuracy and precision for LFB and Matrix Spikes
- Check QCS (second source standards) recoveries
- Check retention time drift
- Check decomposition for Endrin/ DDT
- 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

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- qualifiers
- Check information in the Target Report Header :
  - SOP # & Instrument Serial #
  - Instrument ID
  - Column ID
- Evaluate the data against any field information
- Check LIMS report :
  - preparation and analysis dates
  - MDLs
  - amounts reported for positives
  - qualifiers
  - comments
  - CCV report
  - Method Blank report
  - Surrogate report
  - For more details see DEP SOP OG-003-2, Reference 15.16

11 METHOD PERFORMANCE

11.1 The MDLs are determined by using EPA recommended procedure (40 CFR Pt 136 Appx. B) Ref. 16.3, by analyzing at least 7 spikes in reagent water (water tests) or sodium sulfate (soil, sediment), at 1-5 times the estimated MDL level. The spikes are run and analyzed in DB-5 / DB- 608. The Reported MDLs are chosen based on the highest value measured in the two columns. The equation used to calculate the MDL is as follows:

$$MDL = S\, t_{(n-1,\ 1-a=0.99)}$$

Where: $t_{(n-1,\ 1-a=0.99)}$ is Student coeficient value for the 99% confidence level with
n=number of replicates
S=standard deviation

11.2 The MDLs must be verified annually for each matrix, method, analyte and instrument.

12 DATA ARCHIVAL

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

13 SAFETY

13.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4-DDT,4,4-DDD, BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

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13.2 Lab clothing

13.2.1 Lab coats and safety eyeglasses must be worn at all times when in any laboratory.

13.2.2 Use gloves when handling samples, standards, or solvents, or when washing glassware.

13.3 Chemicals involved

13.3.1 Even though the toxicity or carcinogenicity of some of the reagents used in this method have not been precisely defined, each of them should be treated as a potential health hazard. From this point of view exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

13.3.2 A reference file of Material Safety Data Sheets for each reagents used, is kept in the GC room for documentation. Refer to this folder for any materials you are handling. Update this folder upon receiving new chemicals or reagents.

13.3.3 Primary standards of these toxic compounds should be prepared in a hood (See “Hood Usage”) . A NIOSH/MESA approved toxic gas respirator should be worn when handling highly concentrated solutions of these compounds.

13.4 Waste disposal (see Lab Manual “Laboratory Waste Management” January 2007)

13.4.1 Neat standards should be sealed and labeled.

13.4.2 All stock standards, working standards, and un-used sample extracts must be emptied into two separate waste containers for Pesticides and PCBs. The containers must be labeled properly with hazard warning labels indicating the container contents.

13.4.3 Chlorinated and non-chlorinated solvents must be stored separately and labeled properly.

13.4.4 GC vials containing, standards, and sample extracts, must be stored in two separate waste containers for Pesticides and PCBs. These containers should be labeled properly as to there contents and stored in the hood.

13.4.5 Flammable solvents must be stored in a flammables cabinet.

13.5 Hood Usage

13.5.1 Handle all sample extraction solvent transfers, concentrations, sample preps, and cleanups in the hood at all times.

13.5.2 At any time, no more than two people can work at each hood.

13.5.3 Turn the hood on and wait for adequate airflow. If there is no flow, DO NOT USE THE HOOD!

13.5.4 Only one person should operate the tumbler (per extraction).

13.5.5 Before turning on the tumbler, check all caps and latches for proper closure.

13.5.6 After venting (carefully and slowly!), pull the sash down lower than the separatory funnels. Leave it down until the tumbler comes to a complete stop.

13.5.7 Keep hands and feet clear of the tumbler until it is safe to raise the sash. If positional adjustments of the tumbler are necessary, perform them manually.

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13.6 Glassware

13.6.1 Inspect every piece of glassware to be used. Do not use any that are chipped, cracked, etched, or scratched.

13.6.2 Dispose of all unwanted, broken glassware in the blue "GLASS" box. One should discriminate between "unwanted, broken" glassware and that which is only slightly damaged and reasonably easily repairable.

13.7 For more details see DEP SOP OG-001-3 (Reference 15.18)

14 POLLUTION PREVENTION

14.1 Standards, QC Samples, and Sample Extracts are disposed following laboratory protocol for hazardous waste disposal (see 15.18).
14.2 Contaminated samples, and all other disposed chemical wastes are sent to specialized company for incineration.

15 REFERENCES

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

15.2 EPA 8081B Organochlorine Pesticides by Gas Chromatography; Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW 846; 3rd Edition, Update 4, January 3, 2008.

15.3 EPA 8082A Polychorinated Biphenys (PCBs) by Gas Chromatography; Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, SW 846; 3rd Edition, Update 4, January 3, 2008.

15.4 EPA 608. Methods For Organic Chemical Analysis Of Municipal And Industrial Wastewater. Organochlorine Pesticides And PCBs. 40 C.F.R. Appendix To Part 136, 2008

15.5 6630B &C Liquid-Liquid Extraction Gas Chromatographic Method, Organochlorine Pesticides: Standard Methods For Examination Of Water And Wastewater 18th Edition 1992

15.6 ASTM D 5812, Standard Test Method for Determination of Organochlorine Pesticides in Water by Capillary Column Gas Chromatography, 2002.

15.7 Insecticides in water (Gas Chromatographic Method), Supplement to the Fifteen Edition of Standard Methods for the Examination of Water and Wastewater: Selected Analytical Methods Approved And Cited By The United States Environmental Protection Agency, 1980.

15.8 Methods for the determination of organic substances in water and fluvial sediments, Techniques of Water-Resources Investigations of the United States Geological Survey, USGC Book 5, Chapter 3 , 1987.

15.9 Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol, and Pesticides in Water and Wastewater, USEPA September 1978.

15.10 DEP SOP CM-015-1, Ezchrom Elite Client/Server Chromatography Data System.

15.11 DEP SOP CM-016-1, Target Chromatography Software.

15.12 DEP SOP GC-003-2, Glassware Cleaning Protocol in the Organic Preparations Laboratory

15.13 DEP SOP GC-002-2, Extraction of Organophosphorus, Organonitrogen, Organohalide, and PCBs from Water, Wastes, Sediment, PUFs, and Filters for Subsequent Analysis by GC or GC/MS Techniques..

15.14 DEP SOP LB-027-1, Standard Operating Procedure for Reporting Qualified Data.

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15.15 DEP SOP GC-001-2, Quality Assurance/Quality Control in the GC Pesticides Laboratory.

15.16 DEP SOP OG-003-2, Data Review and Authorization Checklist for GC Pesticides and Associated Sample Preparation.

15.17 DEP SOP GC-013-2 Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in fish tissue by Gas Chromatography with Electron Capture Detection (GC-ECD).

15.18 DEP SOP OG-001-3; Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories)

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

15.20 EPA 608.1 The determination of Organochlorine Pesticides in Municipal and Industrial Wastewater.

15.21 EPA 608.2 The determination of Certain Organochlorine Pesticides in Municipal and Industrial Wastewater.

15.22 EPA 617 The Determination of Organohalide Pesticides and PCBs in Municipal and Industrial Wastewater.

15.23 EPA Determination of Dinitroaniline Pesticides in Municipal and Industrial Wastewater.

16 APPENDICES

16.1 APPENDIX 1

Standards 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# 76827

76827- PSCL_TQ ICV L6
- 76812-PSCL_TQ_ ICV INT
  - 75889-ECD A
  - 75885-ECD B STOCK
- 76629-CL_MS_ISTD_ lOO_ PPM
  - 76628-CL_MS_ISTD_STOCK
    - 68086-CL_ MS_ ISTD_STOCK
      - 68083-A-BHC-D6 NEAT
      - 68082-DDT-DB
      - 66960-HCB-D3 NEAT
      - 66959-TCB-DS NEAT
      - 66958-DCB-DS NEAT

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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, additional concentration levels, etc.

All freshly prepared standards need to be entered in the Standard Preparation Tracker.

Appendix 2

TABLE A METHODS FOR ANALYSIS OF PESTICIDES AND PCBs IN WATER AND WASTEWATER.

PARAMETER	40CFR PART 136 APPROVED METHODS FOR PESTICIDES (TABLE ID)						METHODS ***NOT*** APPROVED IN 40CFR 136		DEP SOP GC-002-2/ GC-011-5 EPA APPROVED as ATP for CWA PROJECTS
	EPA 608 (ref. 15.4)	SM 6630 B (ref. 15.5)	ASTM D5812-96 (ref. 15.6)	15th SM edition Supplement (ref.15.7)	USGS (ref.15.8)	EPA (ref.15.9)	EPA 600 SERIES	WS-846 8081 (ref.15.2)	
Aldrin	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Alpha-BHC	**Y**	*Y*	*Y*			*Y*	617	**Y**	Y
Beta-BHC	**Y**	*Y*	*Y*				617	**Y**	Y
Delta-BHC	**Y**	*Y*	*Y*				617	**Y**	Y
Gamma-BHC	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Carbophenothion				*Y*	*Y*		**617**	**Y**	Y
Chlordane	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Alpha-Chlordane							**1656**	**Y**	*
Gamma-Chlordane							**1656**	**Y**	*
Chlorothalonil			*Y*				**608.2**	**Y**	*
Cypermethrin								**Y**	*
DDD-4,4'	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
DDE-4,4'	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
DDT-4,4'	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Dicofol							**617**	**Y**	Y
Dieldrin	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Endosulfan I	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Endosulfan II	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Endosulfan Sulfate	**Y**	*Y*					617	**Y**	Y
Endrin	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Endrin Aldehyde	**Y**						617	**Y**	Y
Endrin Ketone							**1656**	**Y**	*
Heptachlor	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Heptachlor Epoxide	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Hexachlorobenzene								**Y**	*
Methoxychlor		*Y*	*Y*		*Y*	*Y*	**617**	**Y**	Y
Mirex		*Y*			*Y*	*Y*	**617**	**Y**	Y
Permethrin			*Y*				**608.2**	**Y**	*
Toxaphene	**Y**	*Y*	*Y*		*Y*	*Y*	617	**Y**	Y
Trifluralin		*Y*	*Y*			*Y*	627/**617**	**Y**	Y
PCB-1016	**Y**					*Y*	*617*	**Y**	Y
PCB-1221	**Y**					*Y*	*617*	**Y**	Y
PCB-1232	**Y**					*Y*	*617*	**Y**	Y
PCB-1242	**Y**					*Y*	*617*	**Y**	Y
PCB-1248	**Y**					*Y*	*617*	**Y**	Y
PCB-1254	**Y**					*Y*	*617*	**Y**	Y
PCB-1260	**Y**					*Y*	*617*	**Y**	Y

*Due to missing in 40 CFR 136 list of parameters, formally not approved, but considered as a logical and appropriate extension of the GC/ECD methodology.

The methods used for performance criteria were highlighted in **BOLD**

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Table B M**ethod performance criteria**

Parameter	Performance requirements					Initial Calibration		40 CFR 136 approved
	CV %Rec.	Surr. %Rec.	LCS/MS %Rec.	LCS/MS %RPD	Endrin/DDT% Dec.	Minimum Cal Levels	Linearity criterion	
EPA 608 (Ref 15.4)	+/- 15	N	Lab Stat	N	N	3	10% rsd	Y
EPA 608.1 (Ref 15.20)	+/- 10	N	Lab Stat	N	N	3	10% rsd	N
EPA 608.2 (Ref 15.21)	+/- 10	N	Lab Stat	N	N	3	10% rsd	N
SM 6630 B (Ref 15.5)	N	N	N	N	N	N	N	Y
SM 6630 C (Ref 15.5)*	+/- 15	N	Lab Stat	N	N	3	10% rsd	Y
ASTM D5812-96 (Ref 15.6)	N	N	Lab Stat	Lab Stat	20/20	3	10% rsd	Y
USGS (Ref 15.8)	N	N	N	N	N	N	N	Y
EPA (Ref 15.9)	N	N	Lab Stat	Lab Stat	N	N	N	Y
EPA 617 (Ref 15.22)	+/- 10	N	Lab Stat	Lab Stat	N	3	10% rsd	N
EPA 1656 (Ref 15.23)	Table 4	40-120	Lab Stat	Lab Stat	20/20	3	20% rsd	N
EPA 627 (Ref 15.24)	+/- 10	N	Lab Stat	Lab Stat	N	3	10% rsd	N
EPA 8081 (Ref 15.2)	+/- 15	Lab Stat	Lab Stat	Lab Stat	15	5	20% rsd 0.995 cc	N
EPA 8082 (Ref 15.3)	+/- 15	Lab Stat	Lab Stat	Lab Stat	N	5	20% rsd 0.995 cc	N
DEP SOP GC-011-5	+/-10 / 15	Lab Stat	70-130	</=30	15	5	10/20% rsd 0.995 cc	N

N- Not specified
*Equivalent to EPA 608

Table C M**ethods performance criteria for water test methods used in DEP SOP GC-011-5.**

Parameter	Method	Performance requirements					Initial Calibration	
		CCV %Rec.	Surrogates %Rec.	LCS/MS %Rec.*	LCS/MS %RPD	DDT/Endrin %Dec.	Minimum Cal Levels	Linearity criterion
Aldrin	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Alpha-BHC	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Beta-BHC	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Delta-BHC	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Gamma-BHC	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Carbophenotion	EPA 617	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Chlordane	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Alpha-Chlordane	GC-011-5	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Gamma-Chlordane	GC-011-5	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Chlorothalonil	EPA 608.2	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Cypermethrin	GC-011-5	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
DDD-p,p’	EPA 608	+/-15	Lab Stat	70-130	</= 30	15	5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
DDE-p,p’	EPA 608	+/-15	Lab Stat	70-130	</= 30	15	5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
DDT-p,p’	EPA 608	+/-15	Lab Stat	70-130	</= 30	15	5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Dicofol	EPA 617	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Dieldrin	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Endosulfan I	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd

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Parameter	Method	Performance requirements					Initial Calibration	
		CCV %Rec.	Surrogates %Rec.	LCS/MS %Rec.*	LCS/MS %RPD	DDT/Endrin %Dec.	Minimum Cal Levels	Linearity criterion
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Endosulfan II	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Endosulfan Sulfate	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Endrin	EPA 608	+/-15	Lab Stat	70-130	</= 30	15	5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Endrin Aldehyde	EPA 608	+/-15	Lab Stat	70-130	</= 30	15	5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Endrin Ketone	GC-011-5	+/-15	Lab Stat	70-130	</= 30	15	5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Heptachlor	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Heptachlor Epoxide	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Hexachlorobenzene	GC-011-5	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Methoxychlor	EPA 617	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Mirex	EPA 617	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1016	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1221	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1232	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1242	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1248	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1254	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
PCB 1260	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8082A	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Permethrin	608.2	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Toxaphene	EPA 608	+/-15	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd
Trifluralin	EPA 617	+/-10	Lab Stat	70-130	</= 30		5	10% rsd
	EPA 8081B	+/-15	Lab Stat	70-130	</= 30		5	20% rsd

- *Statutory limits for LFB/matrix spike recoveries are used for most analytes. For analytes not conforming to those limits the recovery limits are derived from statistical data covering the last 5 years of LFB recoveries (see table 6 for details)

Table 1 GC OPERATING PARAMETERS FOR GC/ECD ANALYSIS FOR **HP 6890/7890**

GC PARAMETER	**SETTING**	**GC PARAMETER**	**SETTING**
Temperature 1	80 degree C	Injector Temperature	220 degree C
Time 1	1 minute	Detector Temperature	325 degree C
Ramp 1	30 degree C/min	Carrier Gas	Helium
Temperature 2	190 degree C	Initial Column Pressure	10 psi
Time 2	0 minute	Column Flow Rate	1.43 mL/Min in both
Ramp 2	3.6 degree C/min	Septum Purge Flow Rate	3 mL per minute
Temperature 3	250 degree C	Make up Gas	Nitrogen
Time 3	2.67minutes	Make up Gas Flow Rate	60 mL per minute

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GC PARAMETER	SETTING	GC PARAMETER	SETTING
Ramp 3	15 degree C/min	Column Mode	Constant flow
Temperature 4	280 degree C	Initial flow	1.9 mL/min
Time 4	11 minutes	R T Window	0.070 minute
Total Run Time	37 minutes	Split Mode	Splitless/1 min/15 mL/min/0.5-1.0 uL
Equilibration Time	1 minute	Gas saver	17 mL/min/@2min

(NOTE: The operating parameters for both columns are the same).

TABLE 2 GC AUTOSAMPLER OPERATING PARAMETERS FOR GC/ECD ANALYSIS

Autosampler Parameter	Setting	Autosampler Parameter	Setting
Inj/Bottle	1	Volume (for syringe 5 uL)	1- 2
First Bottle	1	# of Solvent A washes	6 (Acetone)
Last Bottle	100	# of solvent B washes	6 (Iso-Octane)
# of Sample washes	2	Priority Sample (1=Yes)	No
# of Pumps	6	Capillary On-Column	No
Viscosity	1		

TABLE 3 METHOD DETECTION LIMITS AND PRACTICAL QUANTITATION LIMITS FOR GC/ECD ANALYTES

COMPONENT	MDL	PQL
	ug/L	ug/L
aldrin	0.0020	0.0080
alpha-BHC	0.0020	0.0080
beta-BHC	0.0020	0.0080
gamma-BHC	0.0020	0.0080
delta-BHC	0.0020	0.0080
carbophenothion	0.0060	0.024
chlordane technical	0.020	0.080
alpha-chlordane	0.0020	0.0080
gamma-chlordane	0.0020	0.0080
chlorothalonil	0.0080	0.032
cypermethrin	0.012	0.048
DDD-4,4’	0.0040	0.016
DDE-4,4’	0.0040	0.016
DDT-4,4’	0.0040	0.016
dicofol	0.024	0.096
dieldrin	0.0020	0.0080
endosulfan I	0.0020	0.0080
endosulfan II	0.0020	0.0080
endosulfan sulfate	0.0040	0.016
endrin	0.0064	0.026
endrin aldehyde	0.0040	0.016
endrin ketone	0.0040	0.016
heptachlor	0.0020	0.0080
heptachlor epoxide	0.0020	0.0080
hexachlorobenzene	0.0020	0.0080
hexachlorocyclopentadiene	0.0080	0.032
methoxychlor	0.010	0.040
mirex	0.0060	0.024
pcb 1016	0.020	0.080
pcb 1221	0.020	0.080

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COMPONENT	MDL	PQL
pcb 1232	0.020	0.080
pcb 1242	0.020	0.080
pcb 1248	0.020	0.080
pcb 1254	0.020	0.080
pcb 1260	0.020	0.080
permethrin	0.010	0.040
toxaphene	0.10	0.40
trifluralin	0.0080	0.032

TABLE 4 CONCENTRATION LEVELS OF GC/ECD ANALYSIS STANDARDS (ug/L)

Parameters	Intermediate	Dil 1	Dil 2	Dil 3	Dil 4	Dil 5	Dil 6	Spike solution (ug/L)
ECD A MIXTURE								
Aldrin	1,000	50	37.5	25	10	4	2	100
Alpha-BHC	1,000	50	37.5	25	10	4	2	100
Alpha-Chlordane	1,000	50	37.5	25	10	4	2	100
Beta-BHC	1,000	50	37.5	25	10	4	2	100
Delta-BHC	1,000	50	37.5	25	10	4	2	100
Gamma-BHC	1,000	50	37.5	25	10	4	2	100
Gamma-Chlordane	1,000	50	37.5	25	10	4	2	100
DDD-p,p’	1,000	50	37.5	25	10	4	2	100
DDE-p,p’	1,000	50	37.5	25	10	4	2	100
DDT-p,p’	1,000	50	37.5	25	10	4	2	100
Dieldrin	1,000	50	37.5	25	10	4	2	100
Endosulfan I	1,000	50	37.5	25	10	4	2	100
Endosulfan II	1,000	50	37.5	25	10	4	2	100
Endosulfan Sulfate	1,000	50	37.5	25	10	4	2	100
Endrin	1,000	50	37.5	25	10	4	2	100
Endrin Aldehyde	1,000	50	37.5	25	10	4	2	100
Endrin Ketone	1,000	50	37.5	25	10	4	2	100
Heptachlor	1,000	50	37.5	25	10	4	2	100
Heptachlor Epoxide	1,000	50	37.5	25	10	4	2	100
Methoxychlor	5,000	250	187.5	125	50	20	10	500
Tetrachloro-m-Xylene	1,000	50	37.5	25	10	4	2	200
Decachlorobiphenyl	1000	50	37.5	25	10	4	2	200
ECD B MIXTURE								
Carbophenothion	1000	50	37.5	25	10	4	2	200
Chlorothalonil	1000	50	37.5	25	10	4	2	200
Cypermethrin	5,000	250	187.5	125	50	20	10	1000
Dicofol	5,000	250	187.5	125	50	20	10	1000
Mirex	2,000	100	75	50	20	8	4	200
Permethrin	5,000	250	187.5	125	50	20	10	1000
Trifluralin	1000	50	37.5	25	10	4	2	200
Hexachlorobenzene	1000	50	37.5	25	10	4	2	200
PCB 1221+1254 MIXTURE								
Aroclor 1221	10,000							2500
Aroclor 1254	10,000							2500

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PCB 1016+1260 MIXTURE								
Aroclor 1016	10,000			500				2000
Aroclor 1260	10,000			500				2000
Chlordane Technical	10,000	1,000	750	500	250	80	40	200
Toxaphene Technical	10,000	5,000	2,000	1,000	600	300	200	8,000
Aroclor 1016	10,000	1,000	750	500	250	80	40	2000
Aroclor 1221	10,000	1,000	750	500	250	80	40	2000
Aroclor 1232	10,000	1,000	750	500	250	80	40	2000
Aroclor 1242	10,000	1,000	750	500	250	80	40	2000
Aroclor 1248	10,000	1,000	750	500	250	80	40	2000
Aroclor 1254	10,000	1,000	750	500	250	80	40	2000
Aroclor 1260	10,000	1,000	750	500	250	80	40	2000

TABLE 5 RECOVERY AFTER SULFURIC ACID CLEAN-UP

Parameter	Sulfuric acid Clean-up	Parameter	Sulfuric acid Clean-up
Aldrin	Non-resistant	Benfluralin	Non-resistant
Alpha-BHC	Resistant	Alpha-Chlordane	Resistant
Beta-BHC	Resistant	Endrin	Non-resistant
Delta-BHC	Resistant	Chlordane	Resistant
Gamma-BHC	Resistant	PCB-1016	Resistant
DDD-p,p'	Resistant	PCB-1221	Resistant
DDD-o,p'	Resistant	PCB-1232	Resistant
DDE-p,p'	Resistant	PCB-1242	Resistant
DDE-o,p'	Resistant	PCB-1248	Resistant
DDT-p,p'	Resistant	PCB-1254	Resistant
DDT-o,p'	Resistant	PCB-1260	Resistant
Dieldrin	Non-resistant	Toxaphene	Resistant
Endosulfan I	Non-resistant		
Endosulfan II	Non-resistant		
Endosulfan Sulfate	Non-resistant		
Endrin Aldehyde	Non-resistant		
Heptachlor	Resistant		
Heptachlor Epoxide	Non-resistant		
Methoxychlor	Non-resistant		
Carbophenothion	Non-resistant		
Chlorobenzilate	Non-resistant		
Chlorothalonil	Non-resistant		
Cypermethrin	Non-resistant		
Dicofol	Resistant		
Endrin Ketone	Non-resistant		
Gamma-Chlordane	Resistant		

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Isodrn	Non-resistant		
Mirex	Resistant		
PCNB	Resistant		
Permethrin	Non-resistant		
Trans-Nonachlor	Resistant		
Hexachlorobenzene	Resistant		
Hexachlorocyclopentadiene	Non-resistant		
Trifluralin	Non-resistant		

TABLE 6: QC MEASUREMENTS AND ACCEPTANCE CRITERIA

#	QC MEASUREMENT	ACCEPTANCE CRITERION		CORRECTIVE ACTION
		CWA (NPDES)	RCRA	
1	LFB/Matrix spike* recoveries Endrin Dicofol Hexachlorobenzene Methoxychlor	70-130 % 78-147% 26-204% 55-107% 81-151%	70-130 % 78-147% 26-204% 55-107% 81-151%	Reanalyze/Re-extract/Flag/Comment
2	LFB/MS precision	=/< 30 %	=/< 30 %	
3	Cal. Verification	+/-15% +/- 10%	+/- 15 %	Re-run and recalibrate/Flag/Comment
4	Surrogate recovery TMX DCB	 39-129% 43-136%	 39-129% 43-136%	Reanalyze/Re-extract/Flag/Comment
5	QCS verification	+/- 15%	+/- 15%	Re-run and recalibrate/Flag/Comment
6	Instrument performance	Annual MDL verification For more details see DEP SOP GC-001-2 (Reference 15.15)	Annual MDL verification For more details see DEP SOP GC-001-2 (Reference 15.15	Maintain and re-run
7	Calibration Levels Calibration Fit Acceptance criterion	3 levels linear 10%RSD	5 levels Linear, 6 levels quad 20% RSD 0.995 CC	Use appropriate cal fit / Re-run/ Recalibrate/Flag/Comment
8	Lowest calibration point re-fitting	+/- 20% of expected v	+/- 20% of expected value	Use appropriate cal fit/Re-run/ Recalibrate/Flag/Comment

* Statutory limits are used for assessing LFB/matrix spike recoveries. The limits are verified annually based on statistical data. Statistical limits are used whenever they differ significantly from the statutory limits.

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APPENDIX OF SIGNIFICANT CHANGES

10/16/2013	Language describing differences between CWA (NPDES) and RCRA methods has been modified. Requirement for six levels for quadratic calibration have been added. The statistical limits formula for surrogate recoveries have been updated. Updated standard preparations;ECDC Mix removed, replaced with DDT/Endrin decomposition check. Quantification of multicomponent analytes has been clarified. Run sequence updated to place CCVs just before the samples. Spike recoveries for CWA water samples tightened to reflect EPA 608 requirements; QC tables updated
01/09/2014	Updated QC acceptance criteria in Table 6, updated standard concentrations in table 4.
01/05/2015	Chapter 9.1.3 was added describing troubleshooting after runs with poor data quality. Removed soil/waste analysis due to dropping the tests/certification Changes in standards concentrations and mixes composition Changes in QC acceptance criteria based on current statistics Updates to standards preparation procedure
02/11/2015	Statutory recovery limits for spikes and LFBs set to 70-130% for both CWA and RCRA analysis.
01/04/2016	Updated recovery limits (table C and table 6)
01/04/2017	Updated recovery limits (table 6). Removed RCRA tests for water samples due to transfer of those analysis to GC/MS. Tests W-PST-CL-R and W-PCB-R will be closed in LIMS. Removed references to EPA 1656; replaced with this SOP GC-011-5 for Alpha-Chlordane, Gamma-Chlordane and Endrin Ketone. Those analytes are not listed under CWA and they are not routinely analyzed under W-PC-AA-SF (not in default sublist). Updated Appendix 1; Standard preparation procedure. Updated standard concentration table. Added prohibition for “include origin’ in calibration fits.
12/21/2017	Added requirement to always run full calibration for PCB-1016+1260, modified the run sequence to reflect that requirement.
01/02/2018	Edited tables. Updated QC limits. Edited run sequence to add full calibration for PCB-1060.. Added short description of Methoxychlor/Dicofol coelution in DB-5.

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