ROUTINE ANALYSIS OF PESTICIDES IN WATER SAMPLES BY GC/ECD

(EPA/SW-846 Methods 3500B/3510C/8000B/8081A)

(EPA/SW-846 Methods 3600C/3620B/3640A/3660B - Optional)

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* These sections affected by Revision 2.0.

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SUPERSEDES: SOP #1808; Revision 1.0; 11/27/05; U.S. EPA Contract EP-W-09-031.

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the determination of organochlorine pesticides with the possible presence of polychlorinated biphenyls (PCBs) or toxaphene in a water matrix, using a gas chromatograph (GC) with a narrow-bore fused silica column and an electron capture detector (ECD). This SOP is based on Environmental Protection Agency (EPA) Methods SW846/3500B/3510C/8000B/8081A and those requirements set forth in the latest approved version of the National Environmental Laboratory Accreditation Committee (NELAC) Quality Systems section. Extracts may be subjected to optional cleanup procedures (florisil, gel permeation chromatography [GPC], tetrabutylammonium [TBA] sulfite or activated copper powder) based on EPA/SW-846 Methods 3600C/3620B/3640A/3660B. The compounds of interest and typical reporting limits (RLs) in water matrices are found in Table 1, Appendix A.

This method may not be changed without the expressed approval of the Organic Group Leader, the Analytical Section Leader and the Quality Assurance Officer (QAO). Only those versions issued through the SERAS document control system may be used. Modifications made to the procedure due to interferences in the samples or for any other reason must be documented in the case narrative and on a nonconformance memo.

2.0 METHOD SUMMARY

Approximately 1 liter (L) of a water sample is extracted in methylene chloride. The extract is concentrated to 10 milliliters (mL), then 60 mL of hexane is added as an exchange solvent, and the extract is concentrated to a final volume of 1 mL. The extracts are analyzed for pesticides using GC/ECD. Second column confirmation is required for the confirmation of single component pesticides but not required for multi component compounds such as PCBs or toxaphene analysis.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

3.1 Sample Storage

Water samples should be collected in 1-liter (L) amber glass containers fitted with Teflon®-lined caps. From the time of collection until after analysis, extracts and unused samples must be protected from light and refrigerated at 4 ± 2 degrees Celsius (°C) for the periods specified by SERAS Task Leader (TL) and/or the Work Assignment Manager (WAM) for the project.

Samples and sample extracts must be stored separately from standards in an atmosphere free of all potential contaminants.

3.2 Holding Times

The extraction of water samples will be completed within seven days of sample collection and

analysis completed within 40 days of sample extraction.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences in the sample extracts for analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks on a routine basis. Interferences co-extracted from the samples may vary considerably from sample to sample. Cleanup procedures may be necessary if the extract contains analytes that interfere with quantitation or peak separation.

Phthalate esters are present in many types of products commonly found in the laboratory. Some plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

Elemental sulfur is encountered in many sediment samples such as marine algae and some industrial wastes. Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors. If the GC is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through the aldrin peak. Three techniques, GPC cleanup, activated copper powder, or TBA sulfite for the elimination of sulfur may be used. Florisil cleanup may be used to reduce matrix interferences caused by polar compounds.

5.0 EQUIPMENT/APPARATUS

The following equipment/apparatus is required:

- Waters GPC instrument or equivalent
- Teflon filters, 0.45µm, for filtering extracts for gel permeation chromatography (GPC) cleanup (Gelman Acrodisc CR or equivalent)
- Separatory funnel, 2000 mL with stopcock (glass or Teflon)
- Erlenmeyer flasks, 500 mL
- Buchner funnels
- Bench top shaker (Glas-Col) or equivalent

- Glass wool, Pyrex baked @ 400°C for 2 hours or equivalent.
- Kuderna-Danish (K-D) apparatus, consisting of a 10-mL graduated concentrator tube, 500-mL evaporative flask, and three-ball macro Snyder column
- Water bath , heated with concentric ring cover, capable of maintaining temperature within ±2°C. The bath should be used in a hood.
- Disposable glass Pasteur pipettes
- Nitrogen evaporation device, equipped with a water bath that can be maintained at 35-40°C (N-Evap by Organomation Associations Model Number 111 or equivalent)
- TurboVap concentrator, with concentrator cells and racks
- Clean Bath solution, for use in TurboVap II concentrator
- Vials and caps, 2 mL for GC autosampler
- Vials, 4-mL, for GPC cleanup
- Disposable glass pasteur pipettes
- Florisil cartridge, 12 mL tube (Supelco CAT # 57155 or equivalent)
- Vortex Mix II (120v, 40w, 50/60 Hz) or equivalent
- Test tubes with screw caps, 25 mL
- Gas chromatograph - An analytical system complete with GC and all required accessories including syringes, autosampler, analytical columns, gases, an electron capture detector, and data system. A data system is required for measuring peak areas or peak heights and recording retention times.
- RTX-XLB fused silica capillary column, 30 meter (m) x 0.32 millimeter (mm) inner diameter (ID), 0.50 micron (um) film thickness or equivalent
- RTx- CLPesticides fused silica capillary column, 30 m x 0.32 mm ID, 0.50 um film thickness or equivalent
- Visiprap SPE vacuum manifold, 12 port or equivalent
- Valve liners, disposable or equivalent

- Syringes, various microliters (µL) volumes, for spiking and preparation of standards
- Micro syringes, 10 µL and larger, 0.006 inch ID needle
- Graduated cylinder, 1L, Class A
- pH paper, wide range
- Volumetric flasks, Class A, various volumes ranging from 5 to 500 mL
- Ring stand

6.0 REAGENTS

- Sodium Sulfate, anhydrous granular reagent grade, heated at 400 C for four hours, cooled in a desiccator, and stored in a glass bottle.
- Hexane, pesticide residue analysis grade or equivalent
- Acetone, pesticide residue analysis grade or equivalent
- Methanol, pesticide residue analysis grade or equivalent
- 2-Propanol, pesticide residue analysis grade or equivalent
- Methylene chloride, pesticide residue analysis grade or equivalent
- Tetrabutylammonium sulfite solution - Prepare by dissolving 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL of reagent water. Extract this solution three times with 20 mL portions of hexanes to remove any impurities. Discard the hexane layer and add 25g of sodium sulfite to the aqueous layer. Store this solution at room temperature.
- Sodium hydroxide (NaOH), 10 Normal (N)- Weigh out 40g of NaOH and dissolve in 100mL of deionized water.
- Sulfuric acid (H_2SO_4), 1:1-Add and equal volume of concentrated H_2SO_4 to an equal volume of deionized water.
- Deionized (DI) water, Type II or equivalent
- Copper powder, activated, commercially available

- Pesticide Internal Standard Solution - Prepare a solution containing 4,4'-Dibromooctafluorobiphenyl, 4,4'- Dibromobiphenyl, and 3,3',4,4'-Tetrabromobiphenyl at concentration of 5 microgram/milliliter (µg/mL) in hexane.

- Stock Pesticide Calibration Standard, 200 milligrams/liter (mg/L), commercially available

- Working Pesticide Calibration Standards - Prepare a minimum of five concentration levels at 20, 50, 100, 200, 500 micrograms/liter (µg/L). Each calibration standard must contain all of the compounds listed in Table 1, Appendix A, contain the two surrogates at the same concentrations as the calibration standards, and contain the pesticide internal standard compounds at concentration of 100µg/L. Add 20µL of the 5ppm IS to 1mL for all standards.

- Stock Pesticide Surrogate Standard, 200 mg/L, commercially available

- Working Pesticide Surrogate Solution - Prepare a solution containing decachlorobiphenyl (DCBP) and 2,4,5,6-tetrachloro-meta-xylene (TCMX)at a concentration of 200 ng/mL in methanol or acetone.

- Stock Pesticide Matrix Spike (MS) Solution, 100/200 mg/L, commercially available, source must be independent of the calibration standards

- Working Pesticide MS Solution - Prepare a spiking solution in methanol or acetone that contains the pesticides at the concentrations specified below:

    - gamma-BHC 125 nanograms/milliliter (ng/mL)
    - Heptachlor 125 ng/mL
    - Aldrin 125 ng/mL
    - Dieldrin 250 ng/mL
    - Endrin 250 ng/mL
    - 4,4'-DDT 250 ng/mL

- Stock Toxaphene Calibration Standard, 1000 milligrams/liter (mg/L), commercially available

- Working Toxaphene Calibration Standards - Prepare at a minimum of five concentration levels at 0.5, 1, 2, 5, 10 µg/mL. Each calibration standard must contain toxaphene, the two surrogates at concentrations of 20, 50, 100, 200, 500 µg/L and the pesticide internal standard compounds at concentration of 100 µg/L.

- Stock Toxaphene MS Solution, 1000 mg/L, commercially available, source must be independent of the calibration standards

- Working Toxaphene MS Solution - Prepare a spiking solution in methanol or acetone that contains the toxaphene at 20 mg/L.

- PCB Calibration Standards, refer to SERAS SOP #1801, *Routine Analysis of PCBs in Water and Soil/Sediment by GC/ECD.*

- Stock Resolution Check Mixture, 1 to 10 mg/L, commercially available

- Working Resolution Check Solution - Prepare a mixture of pesticides in hexane or methanol at the concentrations in nanograms/milliliter (ng/mL) listed below from the 1-10 mg/L stock resolution check solution. Spike 20µL of 5ppm IS to a 1mL solution.

  - gamma-Chlordane 20 ng/mL
  - Endosulfan I 20 ng/mL
  - 4,4'- DDE 40 ng/mL
  - Dieldrin 40 ng/mL
  - Endosulfan sulfate 40 ng/mL
  - Endrin ketone 40 ng/mL
  - Methoxychlor 200 ng/mL
  - Tetrachloro-m-xylene 40 ng/mL
  - Decachlorobiphenyl 40 ng/mL
  - Pesticide Internal Standard (3 Compounds) 100 ng/mL

- Stock Performance Evaluation Mix (PEM), 1 to 25 mg/L, commercially available

- Working PEM Solution - Prepare the working PEM in hexane or methanol at the concentration levels listed below using the 1-25 mg/L stock PEM solution. Spike 20µL of 5ppm IS to 1 mL solution.

  - gamma-BHC 20 ng/mL
  - alpha-BHC 20 ng/mL
  - 4,4'-DDT 200 ng/mL
  - beta-BHC 20 ng/mL
  - Endrin 100 ng/mL
  - Methoxychlor 500 ng/mL
  - Tetrachloro-m-xylene 40 ng/mL
  - Decachlorobiphenyl 40 ng/mL
  - Pesticide Internal Standard (3 Compounds) 100 ng/mL

  - **NOTE:** All of the above mentioned standard solutions must be stored at 4°C in tightly capped vials with Teflon liners.

  - **NOTE:** Premixed certified standards will be stored according to the manufacturer's documented storage requirements. These standards may be kept in storage up to the manufacturer's stated expiration date. Once the standard vials are opened, the standards will be stored with minimal headspace in the freezer for a period not to

exceed six months or the manufacturer's expiration date, whichever is less.

- **NOTE:** All calibration standards, surrogates, internal standards, and spiking solutions will be prepared and documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions and Reagents.*

7.0 PROCEDURES

7.1 Sample Preparation and Extraction

1. Transfer the sample container into a fume hood. Mark the meniscus of the sample level with an indelible marker, and pour the sample into a 2-L separatory funnel. Check the pH of the sample with wide range pH paper and record it in the extraction log. If the pH is not neutral, adjust the pH between 5 and 9 with 10 N sodium hydroxide and/or 1:1 sulfuric acid solution. Pour tap water into the sample bottle to the meniscus line. Measure the tap water volume using a 1-L graduated cylinder and record the volume on the extraction log.

2. Prepare a method blank and laboratory control sample (LCS) by measuring out 1-L of deionized water and place it into a 2-L separatory funnel. A method blank and LCS must be prepared for every 20 samples or per batch.

3. Measure out two additional 1-L samples for use as a matrix spike/matrix spike duplicate (MS/MSD) at a rate of one MS/MSD per every 10 samples or 10%.

   NOTE: This sample may be specified on the chain of custody record for this purpose by the SERAS Task Leader.

4. Add 1 mL of the 200 ng/mL surrogate working solution to the method blank, LCS, MS/MSD and all the samples or add sufficient volume to result in a final concentration of 200 parts per billion (ppb) in the final extract.

5. Add 1 mL of the 125/250 ng/mL pesticide matrix spiking solution to the LCS and MS/MSD or add sufficient volume to achieve a final concentration of 125/250 ng/mL in the final extract.

6. Rinse the sample bottle with 60 mL of methylene chloride, transfer the rinsate to the separatory funnel and extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer (typically the bottom layer) to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the extraction chemist must employ mechanical techniques to complete the phase separations. The optimal techniques employed depend upon the sample, and may include stirring, filtration, of the emulsion through glass wool, centrifugation, or other physical means. If using a bench top shaker, vent and release excess pressure, place it on shaker and shake for 5 minutes.

7. Filter the extract (typically the bottom layer) through a funnel containing glass wool and anhydrous sodium sulfate into a 500-mL Erlenmeyer flask. Add a second 60-mL portion of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. After the third extraction, rinse the sodium sulfate in the funnel with sufficient methylene chloride. If using the bench top shaker, shake the sample(s) for 3 minutes for the 2nd and 3rd extractions.

8. If concentrating using a TurboVap apparatus, skip to step 12. Otherwise, assemble a Kuderna-Danish (K-D) apparatus by attaching a 10-mL concentrator tube to a 500-mL evaporation flask. Transfer the extract to the K-D concentrator.

9. Add one or two clean boiling chips to the evaporation flask and attach a three-ball Snyder column. Place the K-D apparatus on a hot water bath (70 to 75°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Add approximately 1 mL of hexane to the top of Snyder column. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid is below 10 mL, add another 60 mL of hexane and evaporate down to below 10 mL. Remove the K-D apparatus, and allow it to drain and cool.

   NOTE: DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS. However, If the extract goes to dryness, document the situation in the extraction log book.

10. Remove the Snyder column; use 1-2 mL of hexane to rinse the flask and its lower joint into the concentrator tube. Remove the concentrator tube and place it onto the N-Evap preheated to 35 C.

11. Evaporate the extract to a final volume of 1 mL. During evaporation rinse the wall of the concentrator tube with 1-2 mL of hexane. Continue with step 14.

    NOTE: DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS. However, If the extract goes to dryness, document the situation in the extraction log book.

12. If using the TurboVap concentrator, fill the TurboVap water bath with approximately one gallon of deionized water mixed with 10-15 drops of Clean Bath solution. Set the water bath temperature at 55 C.

13. Transfer as much of the extract(s) that fit into 200-mL concentrator cell in the hood. Begin concentrating by blowing a gentle stream of nitrogen into the cells so that no solvent is splashed out. As the solvent level is reduced, add any remaining extract, rinse the flask with hexane, and add the rinsate to the concentration cell. Once all the extract has been

transferred to the concentrator cell and the solvent level is well below the 200 mL mark, the flow of nitrogen can be increased to speed up the concentration. Periodically rinse the cell with hexane. Concentrate the extract below 10 mL, add 60 mL of hexane and concentrate it down to a final volume of 1 mL.

NOTE: DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

14. Usually no cleanup is required for water extracts. However, it is possible to have extracts that may require cleanup based on visual observation. In that case, take the 1-mL aliquot of the water sample extract from Steps 11 or 13 which include lab blanks, LCSs, and MS/MSDs and proceed to either the optional Gel Permeation Chromatography Cleanup in Section 7.2, Florisil cleanup described in Section 7.3, optional tetrabutylammonium (TBA)-sulfite cleanup described in Section 7.4. or the optional copper cleanup described in section 7.5 Store the remaining extract(s) at 4 C± 2 C. A combination of several cleanups may be used for a single extract.

NOTE: Record the date and the applicable samples subjected to cleanup on the extraction log.

7.2 Gel Permeation Chromatography Cleanup (Optional)

1. Calibrate the GPC instrument by injecting 10 µL of GPC standard (corn oil, bis (2-ethylhexyl) phthalate, methoxychlor, perylene, and sulfur) and eluting it with methylene chloride to establish collection time window to collect the fraction from the beginning of methoxychlor peak to the end of perylene peak.

2. When the collection time window has been established, inject a methylene chloride blank to make sure all calibration components are washed from the column.

3. Before injecting the samples, dilute the final 1.0 mL volume to 4 mL with methylene chloride including method blanks, LCSs and MS/ MSDs. Filter the 4 mL of extract through acrodisc CR PTFE filter (Gelman, 0.45µm) into a clean 4-mL vial.

4. Load the 4-mL vials which contain pre-filtered extracts onto the autosampler and start the sequence.

5. Collect the cleaned extracts from the fraction collector, transfer to the concentrator tubes and concentrate the extracts to a final volume of 2 mL using TurboVap.

NOTE: GPC Pump flow rate is 5.0 mL/minute
GPC Run time is 25 minutes

7.3 Florisil Cleanup

Florisil cleanup significantly reduces matrix interferences caused by polar compounds.

1. Place one Florisil cartridge into the manifold for each sample extract subjected to cleanup.

2. Prior to the cleanup of samples, the cartridges must be washed with 90:10 hexane/acetone. This is accomplished by passing through at least 10 mL of the hexane/acetone solution through the each cartridge.

NOTE: DO NOT ALLOW THE CARTRIDGES TO DRY AFTER THEY HAVE BEEN WASHED.

3. After the cartridges in the manifold are washed, a rack containing labeled 25-mL concentrator tubes is placed inside the manifold. Care must be taken to ensure that the solvent line for each cartridge is placed inside of the appropriate concentrator tube as the manifold top is replaced.

4. After the concentrator tubes are in place, add approximately 1 mL of the mobile solution (90:10 hexane/acetone) to the florisil bed in the cartridge. Allow the solvent to pass into the sorbent bed and immediately transfer 1 mL from each sample, blank and MS/MSD extract from Section 7.1, Step 14 to the top of the florisil bed in the appropriate florisil cartridge.

5. The pesticide extracts are then eluted through the cartridge with 9 mL of 90:10 hexane/acetone and are collected into the 25-mL concentrator tubes held in the rack inside the manifold. NOTE: Be sure to add the 9 mL of mobile solution immediately after the 1-mL extract crosses the florisil bed.

6. Transfer the concentrator tubes to the TurboVap and concentrate the extracts to a final volume of 1 mL using nitrogen blow down.

7.4 Tetrabutylammonium-Sulfite Cleanup

Elemental sulfur is encountered in many soil/sediment samples. The solubility of sulfur in the extraction and exchange solvents is very similar to the organochlorine pesticides; therefore, the sulfur is extracted along with the pesticides. If the GC is operated under normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through aldrin. This cleanup is used to remove the sulfur interference.

1. Transfer the 1 mL of extract from Section 7.1, Step 14 or Section 7.2, Step 6, to a 25-mL test tube.

2. Add 1 mL of TBA-sulfite reagent and 1 mL of 2-propanol; cap and shake vigorously with a mechanical shaker such as Vortex for at least two minutes. If the sample is colorless or if

the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more TBA-sulfite reagent until a solid residue remains after repeated shaking.

3. Add 6 mL of deionized water and shake for at least two minutes. Allow the sample to stand for 5-10 minutes. Transfer the hexane layer (top) to two 1-mL injection vials. The extracts may be analyzed by GC/ECD.

7.5 Copper Cleanup

Copper cleanup requires that the copper powder be very reactive.

1. Transfer 1 mL of sample extract from Section 7.1 step 14 or Section 7.2, step 6 or Section 7.3 step 3, to a 4-mL screw-top vial.

2. Add approximately 0.5 to 2 g of copper powder (depends on the color and viscosity of sample) to the vial. Vigorously mix the extract and copper powder for at least 1 minute on a mechanical shaker such as Vortex. Allow the copper to settle.

3. Separate the extract from the copper by drawing off the extract with a disposable glass pipet into two 1-mL injection vials.

7.6 GC/ECD Conditions

Sample analyses are performed using a Hewlett Packard (HP) 6890 GC/ECD, equipped with dual injector, column, and electron capture detector capabilities.

The HP 6890 conditions used for the pesticide analysis are listed below:

Injector Temperature	250°C
Oven Temperature Program	120°C hold for 1 minute (min) 9°C/min to 285°C, 10 min at 285°C
Detector Temperature	300°C
Carrier Gas	Helium
Make-up Gas	Argon/Methane
Column Flow Rate	RTX-XLB 3.0 milliliters/minute (mL/min); Rtx-CLPesticides 1.0 mL/min
Amount Injected	1 microliter (uL)
Data System	HP Chem Station

The instrument conditions listed above are guidelines to be used for standards and sample analysis on a HP 6890 GC/ECD system. Any suitable conditions may be used as long as QA/QC criteria and peak separation is achieved.

7.7 Retention Time Windows

Absolute retention times are used for compound identification. Retention time (RT) windows are crucial for the identification of the target compounds. Absolute RT windows must be applied for each analyte and surrogate on each column and instrument. Retention time windows are also established to compensate for shifts in absolute RTs as a result of instrument variability and sample loadings. The RT window must be carefully established to minimize the occurrence of false negatives or false positives.

Due to advances in electronic pressure controls in modern GCs, such as the HP6890, the RTs usually remain constant and may exhibit a negligible shift (nearly zero) over the traditional 72-hour period. A default standard value of ±0.030 minutes will be used for the two surrogates and a value of ±0.020 minutes will be used for the target and internal standard analytes. These default values will be applied unless the instrument and EPC unit cannot maintain constant retention times. An alternate method for determining the retention time windows is detailed in Section 7.6.1. If the instrument cannot maintain reproducible RTs, the analyst must investigate the cause and implement corrective action. Establish the absolute RT for each analyte, surrogate and internal standard from the calibration standard analyzed at the beginning of the analytical sequence. For samples run during the same sequence as the initial calibration, use the RT of the 100 µg/L standard. New RT windows must be calculated whenever a new column is installed.

7.7.1 Alternate Retention Time Window Determination

1. Make three injections of all pesticide standard mixtures over a 72-hour period. The injections may include initial calibration, continuing calibration and end of sequence runs. All standard runs must be included in the RT window calculation unless a poor injection is observed.

2. Calculate the standard deviation (SD) of the absolute retention times for each compound, surrogate and internal standard on both columns. Plus or minus three times the SD obtained during the 72-hour period is defined as the width of the RT window.

7.8 Standard and Sample Analysis

7.8.1 Pesticide Analysis (excluding toxaphene)

The analytical sequence listed in Figure 1, Appendix B must be followed for single component and Figure 2, Appendix B must be followed for multi-component compounds.

1. Inject the working Resolution Check Standard and calculate the percent resolution between peaks.

$$\%\ Resolution = \frac{the\ depth\ of\ the\ valley\ between\ the\ peaks}{peak\ height\ of\ the\ smaller\ peak\ being\ resolved}\ x\ 100$$

The % resolution must be ≥ 60.0% for all peaks to continue the analysis.

2. Inject the working PEM and calculate the percent breakdown (%BD) of 4,4'-DDT and endrin on the primary column by using either the peak height or peak area using the following equations:

$$\%\ DDT\ BD = \frac{Total\ DDT\ in\ degradation\ (DDE + DDD)}{Total\ DDT\ (DDT + DDE + DDD)}\ x\ 100$$

$$\%\ Endrin\ BD = \frac{Total\ endrin\ in\ degradation\ (endrin\ aldehyde + endrin\ ketone)}{Total\ endrin\ (endrin + endrin\ aldehyde + endrin\ ketone)}\ x\ 100$$

The %BD of 4,4'-DDT or endrin must not exceed 15.0%. If the requirement is not met, corrective action (injector maintenance and re-calibration) must be taken before further analyses can continue. If analytes are reported from both columns, the %BD must be supplied for both columns.

3. Prepare calibration standards as in Section 6.0. Inject 1 µL each of the five single component calibration standards and tabulate the peak height or peak area for each standard concentration. Calculate the response factor (RF) for each compound at each standard concentration. The average RF and percent relative standard deviation (%RSD) must also be calculated for both columns using the equations below.

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_X = Area or Height of the characteristic ion of each target analyte
A_{IS} = Area of the characteristic ion of each internal standard assigned to target analytes
C_{IS} = Concentration of each internal standard (ng/mL)
C_X = Concentration of each target analyte (ng/mL)

$$RF_{avg} = \frac{RF_1 + \ldots + RF_5}{5}$$

$$SD = \sqrt{\frac{\sum_{i=1} - }{N-1}}$$

$$SD = \sqrt{\frac{\sum_{n=1} RF_i - RF_{average}}{4}}$$

$$\%RSD = \frac{SD}{RRF_{average}} \times 100$$

4. Alternate External Standard Method

   Prepare calibration standards as in Section 6.0. Inject 1 µL each of the five single component calibration standards and tabulate the peak height or peak area for each standard concentration. Calculate the response factor (RF) for each compound at each standard concentration using the equation below. The average RF and %RSD must also be calculated for both columns using the equations above in Section 7.8.1 Step 3.

$$RF = \frac{Peak\ Area\ or\ Peak\ Height\ of\ the\ Analyte}{Mass\ Injected\ (pg)}$$

   The %RSD for each analyte must be ≤ 20% for the internal standard method and external standard method. If analytes are reported from both columns, the %RSD must be supplied for both columns. If the %RSD fails the criteria for any of the compounds, the analyst may employ linear regression or a quadratic equation. The value of R^2 must be >0.98.

   NOTE: An initial calibration curve must be run every six months at a minimum or sooner if the daily calibration check doesn't meet the required percent difference (%D) as specified in Section 7.8.1, Step 6.

5. Inject 1 ppm each of Aroclor (Ar) 1016, Ar 1232, Ar 1242, Ar 1248, Ar 1254,

Ar 1260, Ar 1268 and 2 ppm each of Ar 1221 and toxaphene as fingerprints.

NOTE: The fingerprints are used for qualitative pattern matching only. The fingerprints are not run with each initial calibration curve as long as the date of the fingerprints do not exceed one year or a new source of standards is received.

6. For every 12 hours of sample analysis, inject the 100 µg/L continuing calibration standard, which is mid-point of the curve. Calculate the %D of each compound in the mixture using the following equation:

$$Percent\ Difference(\%D) = \frac{ARF_{INT} - RF_{CALC}}{A_{INT}} x\ 100$$

where:

ARF_{INT} = Initial Average Response Factor
RF_{CALC} = Calculated Response Factor

The %D must be ≤15.0% for all compounds.

7. Inject a group of sample extracts. It is recommended to inject the method blank and LCS first. All sample extracts must be analyzed within 12 hours of the injection of the PEM or the midpoint standard.

8. At the end of the 12-hour period, inject a 100 µg/L pesticide standard as another calibration verification. Calculate and tabulate the %D of all compounds. If all compounds have a %D ≤15.0%, proceed to step 9. If not, necessary maintenance must be performed on the instrument prior to the analysis of any other sample extracts. The sequence must be started from step 6. For additional criteria, refer to Section 9.0.

9. Inject another group of sample extracts. The extracts must be injected within 12 hours of the injection of the 100 µg/L standard described in step 8. The sequence will end with the last injection of the 100 µg/L continuing calibration standard. The %D criteria must be met prior to injecting any further sample extracts.

7.8.2 Toxaphene Analysis

Identify the presence of toxaphene in the samples extracts using the toxaphene fingerprint standard run in Section 7.8.1, step 5.

1. Inject each of the five toxaphene calibration standards and choose 5 peaks in each standard to calculate RFs. If the toxaphene pattern changes from standard to

standard or sample to sample, then the total area of all toxaphene peaks will be summed up in order to calculate the average RF. The decision which method to use (5 peaks or total toxaphene peaks area) will be left to the discretion of the analyst. The RF and %RSD must also be calculated for each toxaphene peak or total pattern area and surrogates using the equations in Sections 7.8.1 Step 3 and 7.8.1 Step 4.

The average of 5 peaks or total toxaphene area %RSD and surrogates must be less than or equal to (≤) 20.0%.

NOTE: The initial curve must be run every six months at a minimum or sooner if the daily calibration check doesn't meet the required percent difference (%D) as specified in Section 7.8.1 Step 6.

2. Every 12 hours of sample analysis, inject the 2 ppm continuing calibration check standard, which is the mid-point of the curve. Calculate and tabulate the %D of all 5 peaks or total toxaphene peaks area and the average the percent difference must be ≤ 15% using the equation in Section 7.8.1 Step 6.

3. Inject a group of sample extracts. It is recommended to inject a method blank and LCS first. All sample extracts must be analyzed within 12 hours of the injection of the continuing calibration standard (step 2).

   Repeat steps 2 and 3, if necessary, until the %D requirement of the continuing calibration check fails.

   End the sequence with the continuing calibration check standard.

7.8.3 PCB Analysis

Identify the presence of PCBs in the sample extracts using the fingerprint chromatograms generated in Section 7.8.1, step 5. If PCBs are present, refer to SERAS SOP #1801, *Routine Analysis of PCBs in Water and Soil/Sediment by GC/ECD* for detailed analysis procedures.

7.9 Evaluation of Chromatograms

All standard and sample chromatograms must be evaluated to determine if re-injection and/or dilution is necessary.

7.9.1 Standard/Sample Chromatograms

The following requirements apply to all data generated for single component or multi

component analytes.

1. The pesticide chromatograms must display the single component analytes and multi component analytes present in each standard or sample at greater than (>) 25% and less than (<) 100% of full scale. The chromatogram must be printed in landscape mode with the time scale of the chromatogram from approximately 5 to 25 minutes (somewhere after the DCBP peak). If the time scale is modified, all chromatograms will be scaled the same for comparative purposes.

2. If an extract is diluted, chromatograms must display single component or multi component pesticides between 10% and 100% of full scale.

3. If a chromatogram is re-plotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

4. If a chromatogram show carryover from a previous injection, subsequent sample extract(s) must be re-analyzed, preferably immediately.

5. The retention time of each single component analyte must fall within the RT windows on both columns as determined in Section 7.8. If the RT window has shifted in the thousandth place (>0.020 but <0.030 for target analytes and >0.030 but <0.040 for surrogates), professional judgement may be used to determine the acceptability of the data. If the RT is shifted by more than ± 0.030 minutes for the target analytes and ± 0.040 minutes for the surrogates, the analytical sequence (acquisition) must be interrupted for corrective action. After corrective action, acquisition of data can be resumed only after an acceptable PEM and 100 ppb pesticide standard is obtained. No retention time window is required for toxaphene analysis since the identification of toxaphene is done by pattern recognition.

6. If it is determined that the matrix may be causing a RT shift, the MS/MSD in conjunction with the original sample chosen for spiking may be used to assess matrix effects.

7. If a sample chromatogram has interfering peaks, a high baseline, or off-scale peaks, the sample extract must be re-analyzed using a dilution or further cleanup techniques. In some instances, re-extraction may be performed. Samples that do not meet acceptance criteria after one re-extraction and cleanup must be reported in the case narrative and do not require further analysis.

8. If there are two peaks within a RT window, the data will be reported from the other column with one peak within the window.

9. If manual integrations have been performed, refer to SERAS SOP #1001, *Chromatographic Peak Integration Procedures* for appropriate documentation

procedures.

7.9.2 Pesticide Identification

The identification of single component pesticides is based primarily on RT data. The retention time of the apex of the peak can only be verified from an on-scale chromatogram. The identification of toxaphene is primarily based on pattern recognition, which can only be verified from an on-scale chromatogram. Second column confirmation is optional for toxaphene analysis.

1. Single component analytes are identified when peaks are observed in the RT windows for the compound on both GC columns. The identification of multi component is primarily based on pattern recognition, which can only be verified from an on-scale chromatogram. Second column confirmation is optional for toxaphene analysis.

2. If a peak is just outside any target compound's RT window, examine the retention time of the closest surrogate, internal standards, matrix spike compounds, and the closest calibration check. Use retention times to evaluate a possible RT shift. Similar RT shifts of target compounds can be expected in some cases.

3. If a sample contains interfering peaks or a high baseline, further cleanup may be necessary. Compound identification on this type of sample may be difficult. Information such as surrogate RT, peak ratio on both GC columns, and sample history must be evaluated for identification purposes.

4. If quantifying on both columns and the RPD >40% for a particular analyte, report the highest concentration and flag as estimated (J) for that analyte only. Calculate the %RPD using the equation in Section 8.4.

7.10 Sample Dilution

Target compound concentrations must not exceed the upper limit of the initial calibration range. If analytes are detected in the extract at a level greater than the highest calibration standard, the extract must be diluted (to a maximum of 1:100,000) or until the analyte response is within the linear range established during calibration. Guidance in performing dilutions and exceptions to this requirement are given below.

1. If the analyst has reason to believe that diluting the final extracts will be necessary based on historical data or visual observation of the extracts, an undiluted run may not be required. However, if no peaks are detected above 25% of full scale on the diluted sample, analysis of a more concentrated sample extract or the undiluted sample extract is required.

2. If the response is still above the highest calibration point after the dilution of 1:100,000, the

analyst should contact the Organic Group Leader immediately for further instruction.

3. The results of the original analysis are used to determine the approximate dilution factor required to bring the largest analyte peak within the initial calibration range.

4. The dilution factor chosen should keep the response of the largest peak for a target compound in the initial calibration range of the instrument.

5. Submit data for any reportable analyses.

6. All chromatograms for the dilution analyses must meet the requirements described in Section 7.10.

8.0 CALCULATIONS

Quantitation of target compounds and surrogates can be performed on any column that passed all the quality control (QC) criteria specified in this SOP. In order to be quantitated, the detector response (peak area or peak height) of all the analytes must lie within the calibration range.

8.1 Reporting Limit for Water

$$RL\ (\mu L) = \frac{C_{STD} \times V_T \times DF}{V_O}$$

where:

C_{STD} = Concentration of the lowest standard in the calibration range (µg/mL)
V_T = Volume of the extract (mL)
DF = Dilution factor
V_O = Volume of water extracted (L)

8.2 Sample Concentration for Water

8.2.1 Internal Standard Method

Identified target analytes will be quantitated by the internal standard method. The internal standard used must be the one nearest the retention time to that of the given analyte listed in Table 2, Appendix A.

Use the following equation to calculate the concentration of the identified analytes using the average relative response factor (RRF) obtained from the initial calibration curve.

$$Concentration\ (\mu\ /L) = \frac{(A_X)(I_S)(V_T)(DF)}{(A_{IS})(RRF_{avg})(V_O)(V_i)}$$

where:

A_X	=	Peak Area or Peak Height of each target analyte
I_S	=	Amount of each internal standard injected (ng)
V_T	=	Volume of the concentrated extract (mL)
DF	=	Dilution factor
A_{IS}	=	Peak Area or Peak Height of each internal standard
RRFavg	=	Average Relative response factor
Vo	=	Volume of water extracted (L)
V_i	=	Injection volume (usually 1 µL)

8.2.2 Alternate External Standard Method

Unusual sample matrices which may interfere with the internal standards, and/or unusual circumstances encountered during sample analysis may warrant the use of the external standard method with the discretion of the Organic Group Leader.

$$Concentration\ (\mu\ /L) = \frac{(A_X)(V_T)(DF)}{(RF_{avg})(V_O)(V_I)}$$

where:

A_X	=	Peak area or peak height for the compound to be measured
V_T	=	Volume of the concentrated extract in microliters (µL)
DF	=	Dilution factor
RF_{AVG}	=	Average response factor
V_O	=	Volume of water extracted in milliliters (mL)
V_I	=	Volume of extract injected in microliters (µL)

For the quantitation of PCB concentrations, refer to SERAS SOP #1801, *Routine Analysis of PCBs in Water and Soil/Sediment by GC/ECD.*

NOTE: If any analytes are detected below the reporting limit at >25% of the reporting limit, report the concentration and flag as estimated (J) otherwise reported as undetected.

8.3 Surrogate Spike Recoveries

$$Percent\ Recovery\ (\%R) = \frac{Q_D}{Q_A}\ x\ 100$$

where:

Q_D = quantity determined by analysis
Q_A = quantity added to sample

8.4 Matrix Spike Recoveries

The percent recoveries and the relative percent difference (RPD) between the recoveries of each of the six pesticide compounds are calculated and reported using the following equation:

$$Matrix\ Spike Recovery (\%R) = \frac{SSR - SR}{SA}\ x\ 100$$

where:

SSR = spike sample result
SR = sample result
SA = spike added

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2}\ x\ 100$$

where:

RPD = relative percent difference
MSR = matrix spike recovery
MSDR = matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference; hence, RPD is always expressed as a positive value.

8.5 Laboratory Control Sample Recoveries

The recoveries of each of the compounds in the LCS solution will be calculated using the following equation:

$$Laboratory\ Control\ Sample\ Recovery\ (\%R) = \left(\frac{LCSR - }{SA}\right) x\ 100$$

where:

LCSR = Concentration of target analyte in LCS
B = Concentration of target analyte in blank
SA = Concentration of spike added

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

9.1 Holding Time

Extraction of water samples must be completed within 7 days of sampling, and analysis completed within 40 days of sample extraction.

9.2 Identification of Target Compounds

Each target compound identified on the primary column within the RT window of a single component pesticide must be confirmed within the compound's RT window on the secondary column in order to be reported. The identification of multi component toxaphene is primarily based on pattern recognition and only reported from the primary column. Second column confirmation is optional for toxaphene analysis.

9.3 GC Column Performance

The resolution check demonstrates that the GC column is capable of chromatographically resolving the pesticide target compounds. The resolution check is not required for the analysis of toxaphene only.

The Resolution Check mixture must be analyzed at the beginning of every initial calibration sequence, on each GC column for the instrument used for pesticide analysis.

1. The percent resolution must be greater than or equal to 60% prior to the analysis of standards, samples or blanks on both columns.

2. The percent resolution must be greater than or equal to 60% prior to the analysis of standards, samples or blanks on both columns.

9.4 Initial Calibration for Target Compounds and Surrogates

Prior to the analysis of any sample, method blank, or MS/MSD, the GC/ECD system must be initially calibrated at a minimum of five concentrations to determine the linearity range for all target compounds and surrogates. If reporting data from only one column, the RSDs will be reported from only that column. If reporting data from both columns, all corresponding calibrations will be required for both columns.

The concentration of all calibration standards that are specified in Section 6.0 must be used.

1. The standards are to be analyzed according to the procedures given in Section 7.7 using the GC operating conditions in Section 7.5.

2. The response factors are determined according to the procedure in Section 7.7.

3. The calibration is evaluated on the basis of the extent of endrin and 4,4'-DDT breakdown, as described in Section 7.8.2. The breakdown of either DDT or endrin must not exceed 15.0%.

4. The initial calibration is also evaluated on the basis of the stability of the response factors of each target compound and surrogate. The %RSD of each target compound must not exceed 20.0%. If the %RSD fails the critera for any of the compounds, the analyst could employ linear regression or quadratic equations. The value of R^2 must be >0.98.

9.5 Continuing Calibration for Target Compounds and Surrogates

Once the GC/ECD system has been calibrated, the calibration must be verified each 12-hour time period during which samples are analyzed. If reporting data from only one column, the %D will be calculated from that column only. If reporting data from both columns, the %Ds will be required for both columns.

1. The continuing calibration is evaluated on the basis of the stability of the instrument response to the target compounds present in the PEM and the mid-point standard.

2. If a specific analyte in the standard analyzed after a group of samples exhibits a response >15.0% and the analyte was not detected in any of the samples, the extracts do not have to be re-analyzed.

3. If the %D exceeds 15.0% for a specific analyte and the analyte is present in the sample extract, re-injection is required to ensure an accurate concentration.

4. If the %D for the end of sequence (EOS) standard exceeds 15.0% for a specific analyte and the analyte is present in the sample, the samples after the last good standard must be re-analyzed in another sequence. If the EOS standard still does not meet acceptance criteria after re-analysis, document the result in the case narrative and further analysis is not required.

9.6 Retention Time Windows

The identification of single component pesticide by GC is based primarily on retention time data. Therefore, the determination of retention time windows is crucial for the production of valid data (Section 7.8). No retention time windows are required for multi-component compounds. Refer to SERAS SOP #1801, *Routine Analysis of PCBs in Water and Soil/Sediment by GC/ECD.*

1. The identification of all target compounds analyzed by this SOP is based on the use of absolute retention time.

2. The retention time window for each target compound is determined in accordance with Section 7.6.

3. The retention time shifts of the internal standard may be used to evaluate the stability of the GC system during the analysis of standards only.

4. Retention time windows must be established on both columns and submitted with the data package to support the pesticide identifications reported.

9.7 Analytical Sequence

The standards and samples analyzed by this SOP must be analyzed in a sequence outlined in Figure 1, Appendix B. This sequence includes requirements that apply to the initial and continuing calibrations, as well as the analysis of samples.

9.8 Method Blank and Laboratory Control Sample

A method blank and LCS is a volume of DI water that is carried through the entire analytical procedure. The volume used for the method blank and LCS must be approximately equal to the volume of the samples associated with the blank. The purpose of the method blank and LCS are to determine if there are any contaminants associated and the proficiency of the process and analysis of samples.

1. A method blank and LCS must be prepared for each group of up to 20 samples extracted at the same time or per batch and analyzed on each GC/ECD system used to analyze samples.

2. A method blank must not contain any of the compounds listed in Table 1, Appendix A at concentrations greater than or equal to ( ) the reporting limit.

3. Samples associated with an unacceptable method blank re-extracted and re-analyzed if sufficient sample mass is available and the holding time has not been exceeded. Otherwise, it will be documented in the case narrative. If contaminants are observed in the method blank but not in the samples, note it in the case narrative and sample re-analysis is not required.

4. When sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the sample cleanup procedure. Method blank must be analyzed on all instruments used for sample analysis, this does not include the dilution run.

5. Method blank results must not be subtracted from any associated samples.

6. Use 70 to 130% for LCS recoveries until ranges are established. LCS % Recovery less than 70% must be reported to the Organic Group Leader.

7. A solvent blank may be used to check for contamination or carryover from a previous sample. If an analyte present in the solvent blank is found in subsequent samples, the samples should be re-analyzed. A solvent blank may also be run prior to any standard

9.9 Surrogate Recoveries

1. Surrogates are added to each sample, blank, LCS, MS, and MSD prior to extraction at the concentrations described in Sections 6.0 and 7.1.

2. The surrogate spike recoveries are calculated according to the procedures in Section 8.3.

3. The quality control limit for both surrogate recoveries is 30 - 150%. These limits are only advisory, and no further action is required if the limits are exceeded. However, frequent failures to meet the limits for surrogate recovery warrant investigation by the laboratory.

9.10 Internal Standards

1. Internal standards must be added to all standards and samples including the lab blanks, LCSs and MS/MSDs to achieve a final concentration of 100 µg/L.

2. The peak height (or area) of the internal standards in each sample must be monitored by the analyst and to assure the height (or area) falls between 50% and 150% of the corresponding internal standard in the daily calibration check. If any the internal standards do not meet the criteria (50% to 150%), then it will be flagged with (*).

   Note: Only the internal standards used to calculate the target compounds will be monitored.

3. If one or more internal standard areas do not meet criteria, the GC system must be inspected for malfunctions and corrections made as appropriate. When corrections are made, re-analysis of all affected samples is required. If re-analysis is not feasible due to matrix interference (i.e., coeluting with IS peak) on both columns, the analyst may choose to dilute the sample to remove the interference instead of re-analyzing.

4. If after re-analysis, the areas for all internal standards meet criteria (between 50% and 150%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only data from the analysis with the ISs within limits are required to be submitted. If re-analysis confirms matrix effects, submit both sets of data but report the initial run.

9.11 Matrix Spike and Matrix Spike Duplicate Analysis

The purpose of spiking target compounds into two portions of a sample is to evaluate the effects of the sample matrix on the methods used in this SOP.

1. The MS/MSD must be prepared with every 10 samples per matrix or per project, whichever is more frequent.

2. The matrix spiking solution specified in Section 6.0 must be used and result in the concentration specified in Section 7.1.

3. The recoveries of the MS compounds are calculated according to the procedures in Section 8.4. The %RPD for each spiked analyte are calculated between the results of the MS and the MSD according to the procedures in Section 8.4.

4. The client-specified MS recovery limits are taken from the CLP Statement of Work (revision 5/99) and are as follows:

   Note: If the laboratory fails to meet the recovery QC limits and the RPD limits on a routine basis, the Organic Group Leader must investigate the cause and take corrective action.

Compound	% Recovery	%RPD
gamma-BHC	56 - 123	15
Heptachlor	40 - 131	20
Aldrin	40 - 120	22
Dieldrin	52 - 126	18
Endrin	56 - 121	21
4,4'-DDT	38 - 127	27

   State in case narrative if recoveries are outside criteria. If more than half of the spiked compounds are out, the MS/MSD should be reanalyzed. A matrix effect is indicated if the LCS data are within limits but the MS/MSD are not. A similar pattern must be observed for both the MS and MSD.

   If the lab fails to meet the QC recovery limits and/or the RPD on a routine basis, the Organics Group Leader must investigate the cause and take corrective action. The MS/MSD must be prepared at the same dilution as the least diluted analysis from which sample results will be reported.

5. The sample and MS/MSD must be analyzed and reported from at the same dilution factor.

6. A MS/MSD must be analyzed every 10 samples or per project. The MS/MSD must be associated with a method blank that meets the criteria in section 9.8, a calibration in sections 9.4 and 9.5. The MS/MSDs should be run on the same 12-hour shift as the sample.

9.12 Initial Demonstration of Capability

Initial proficiency in pesticide and toxaphene analysis must be demonstrated by each analyst initially and each time significant changes are made in the procedure or for instrumentation. Each analyst will generate precision and accuracy data using a reference standard other than the source used for calibration. Four replicate of a well-mixed reference standard is analyzed using the procedures outlined in this SOP. Calculate the average mean in µg/L and the standard deviation (S) in µg/L. The QAO will tabulate the results from all of the analysts per matrix per parameter, and calculate control limits.

9.13 Dilution Analysis

If the concentration of any sample extract exceeds the initial calibration range, that sample extract must be diluted and re-analyzed as described in Section 7.9. If there are no peaks detected above 25% of the full scale in the dilution analysis, a lower dilution of the sample extract must be analyzed.

9.14 Reporting Limit

The lowest concentration of the calibration standard that is analyzed during the initial calibration determines the method reporting limit based on the initial volume of the sample and final volume of extract obtained from the extraction.

9.15 Method Detection Limit Studies

Method detection limit (MDL) studies will be run on an annual basis for the water matrix to verify the minimum concentration that can be measured and reported with 99% confidence. A minimum of seven replicates will be used for the study (EPA 1984).

9.16 Nonconformance Memo

A nonconformance memo will be generated any time an employee notices a deficiency suspected of being a nonconformance. This nonconformance memo will be forwarded to the QAO for verification of corrective action.

10.0 DATA VALIDATION

Data will be assessed in accordance with the guidelines set forth in the most recent version of the SERAS data validation SOPs. However, data is considered satisfactory for submission purposes when ALL the requirements mentioned below are met.

1. All samples must be analyzed as part of a valid analytical sequence, i.e., an acceptable initial calibration, and continuing calibration check at the required frequency.

2. All the QC requirements described in Section 9.0 must be met at all times. Any deviations or anomalous conditions should be discussed with the Organic Group Leader and documented in the case narrative.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to U.S. EPA, Occupational Safety and Health Administration (OSHA) and corporate health and safety practices. More specifically, refer to SERAS SOP #3013, SERAS *Laboratory Safety Program* and SERAS SOP #1501, *Hazardous Waste Management*.

12.0 REFERENCES

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13.0 APPENDICES

A - Table
B - Figure

APPENDIX A
Tables
SOP #1808
January 2006

TABLE 1. Target Compound List and Typical Reporting Limits for Water

COMPOUND	RL[(1)] (µg/L)
α-BHC	0.0200
γ-BHC	0.0200
β-BHC	0.0200
δ-BHC	0.0200
Heptachlor	0.0200
Aldrin	0.0200
Heptachlor epoxide	0.0200
α-Chlordane	0.0200
γ-Chlordane	0.0200
Endosulfan I	0.0200
4,4'-DDE	0.0200
Dieldrin	0.0200
Endrin	0.0200
4,4'-DDD	0.0200
Endosulfan II	0.0200
Endrin aldehyde	0.0200
4,4'-DDT	0.0200
Endosulfan sulfate	0.0200
Methoxychlor	0.0200
Endrin ketone	0.0200
Toxaphene	0.500

(1) RL denotes Reporting Limits

TABLE 2. Target Compound List and Internal Standards

4,4'-Dibromooctafluorobiphenyl (IS)
TCMX
α-BHC
γ-BHC
β-BHC
δ-BHC
Heptachlor
Aldrin
Toxaphene

4,4'-Dibromobiphenyl (IS)
Heptachlor epoxide
α-Chlordane
γ-Chlordane
Endosulfan I
4,4'-DDE
Dieldrin
Endrin
4,4'-DDD

3,3',4,4'-Tetrabromobiphenyl (IS)
Endosulfan II
Endrin aldehyde
4,4'-DDT
Endosulfan sulfate
Methoxychlor
Endrin ketone
DCBP

APPENDIX B
Figures
SOP #1808
January 2006

FIGURE 1. Pesticide Analytical Sequence

Time	Injection #	Material Injected
	1	Resolution Check
	2	Performance Evaluation Mix (PEM)
	3-7	Initial Calibration (5-point)
	8-16	Toxaphene and PCB Fingerprints
0 hr.	17	PEM or 100 ppb Pesticide Standard
	18	100ppb Pesticide Standard or PEM
	19	1st Sample
	:	
	:	Subsequent Samples
	:	
12 hr.	○	Continuing Calibration Check Standard
	:	
	:	Samples
	:	
another 12 hr.	○	Continuing Calibration Check Standard
	:	
	:	Samples
	:	
another 12 hr.	○	Continuing Calibration Check Standard
	:	
	:	Samples
	:	
	etc.	
	last	Continuing Calibration Check Standard

NOTE: All subsequent 12-hour periods are timed from the injection of the PEM or the mid-point calibration standard. The analytical sequence must end with a continuing calibration check standard.

FIGURE 2. Analytical Sequence for Toxaphene Analysis

Time	Injection #		Material Injected
0 hr.	1-5		Toxaphene Calibration (5-point)
12 hr. Sequence	n		1st Sample
	0		2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	n+1		1st Sample
	:		
another 12 hr.	:	○	2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	:		
	:		Samples
	:		
another 12 hr.	:	○	2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	:		
	:		Samples
	:		
another 12 hr.	:	○	2 ppm Toxaphene Continuing Calibration Standard and/or End of Sequence
	:		
	:		Samples :
	etc.		
	last		2 ppm Toxaphene End of Sequence

NOTE: All subsequent 12-hour periods are timed from the injection of the mid-point calibration standard. The analytical sequence must end with a continuing calibration check standard (2 ppm toxaphene). The mid-point calibration standard from the initial calibration curve can be used as the daily check.