

Georgia Department of Natural Resources

Environmental Protection Division Laboratory

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Polychlorinated Biphenyls (PCBs) in Water by Gas Chromatography – EPA Method SW846-8082

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1 Scope and Application

- 1.1 Method SW846-8082 is used to determine the concentrations of various Polychlorinated Biphenyls (PCBs) in surface and ground water. Samples are extracted at neutral pH with methylene chloride then solvent exchanged with hexane. The extract is analyzed by injection into a temperature programmable gas chromatograph with an electron capture detector. Identifications are obtained by analyzing a standard curve under identical conditions used for samples and comparing resultant retention times. Concentrations of the identified components are measured by relating the response produced for that compound to the standard curve response.
- 1.2 PCBs 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 are analyzed by this method. The EPD lab uses PCB 1660 (1016 + 1260) as the primary PCB mix for QC purposes. PCBs 1262 and 1268 may be analyzed for screening purposes only for Hazardous Waste projects as they are not included in the WP Performance Test studies.
- 1.3 This method is restricted to analysts who have completed the requirements of the initial demonstration SOP. Refer to SOP reference 13.1.

2 Definitions

- 2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control definitions.
- 2.2 Refer to GA EPD Laboratory SOP 1-052, Organics Data Validation, online revision.

3 Interferences

- 3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms.
- 3.2 Glassware must be scrupulously cleaned with hot water detergent followed by de-ionized water then rinsed with methanol followed by acetone. The glassware is rinsed again with extraction solvent, methylene chloride, immediately prior to use.
- 3.3 The use of high purity reagents and solvents helps to minimize interference problems.
- 3.4 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes.
- 3.5 Matrix interferences may be caused by contaminants that are co-extracted from the sample.

4 Safety

- 4.1 Refer to Georgia EPD Laboratory Chemical Hygiene Plan, online revision.

5 Apparatus and Equipment

- 5.1 Sample container: 1.0L amber bottle with Teflon-lined caps
- 5.2 Vials: auto-sampler vials, clear, screw top, 2.0mL and 300µL inserts
- 5.3 Volumetric flasks (Class A): various sizes
- 5.4 Micro-syringes: various sizes
- 5.5 Syringes: various sizes
- 5.6 Drying column: Sodium sulfate
- 5.7 Glasswool: Baked at 400°C for 4 hours
- 5.8 Gas chromatograph: capable of temperature programming equipped for split/splitless injection
- 5.9 Mega bore 30m X 0.53mm, Rtx-CLP1 or equivalent (0.32mm may be used)
- 5.10 Mega bore 30m X 0.53mm, Rtx-CLP2 or equivalent (0.32mm may be used)
- 5.11 Electron capture detector
- 5.12 Chromatography software
- 5.13 Separatory Funnel: 2.0L with PTFE stopcock
- 5.14 Separatory Funnel Shaker
- 5.15 Graduated cylinders (Class A): 100mL & 1000mL
- 5.16 Erlenmeyer flasks: 250-300mL
- 5.17 Beakers: various sizes
- 5.18 pH indicator paper: pH range 0-14
- 5.19 Balance: Analytical, capable of accurately weighing to the nearest 0.0001g
- 5.20 Balance: Top-loading, capable of accurately weighing to the nearest 0.01g
- 5.21 RapidVap or similar concentrator with nitrogen blow down and controlled heating capabilities

- 5.22 RapidVap or similar concentration tubes with at least 300mL volume
- 5.23 TurboVap or similar concentrator with nitrogen blow down and controlled heating capabilities
- 5.24 TurboVap or similar concentration tubes with at least 50mL volume
- 5.25 Sample extract vials: 10mL culture tubes with caps
- 5.26 Disposable pipettes and bulbs
- 5.27 Detergent: Steris Labklenz or equivalent

6 Reagents and Standards

- 6.1 Methylene chloride: pesticide grade or equivalent
- 6.2 Hexane: pesticide grade or equivalent
- 6.3 Acetone: pesticide grade or equivalent
- 6.4 Isooctane: pesticide grade or equivalent
- 6.5 Reagent water: Purified water which does not contain any measureable quantities of target analytes or interfering compounds for each compound of interest (deionized, HPLC, Milli-Q or equivalent). Milli-Q water has a resistivity of 18 MΩ·cm or greater at 25°C and a TOC of 50µg/L or less.
- 6.6 Sodium sulfate: granular, anhydrous, certified ACS grade suitable for pesticide residue analysis or equivalent

6.6.1 Sodium sulfate is baked for 4 hours at 450°C then stored in a glass container

6.7 Calibration Standard Solutions

- 6.7.1 Prepare five different concentrations equivalent to the concentration levels in Section 8.2 by dilution of the stock standard solutions. Standard stock solutions are usually at a concentration of 200µg/mL or 1000µg/mL in various solvents or from neat concentration. Calculations or amounts will vary depending on the stock standard concentration. Prepare the primary dilution standard of 200XP at 20µg/mL concentration for PCBs and 0.8-1.6µg/mL for Surrogates.
- 6.7.2 Calibration Standards for each PCB must have a minimum of 3 peaks selected but preferably 5 or more peaks with the exception of PCB 1221 which only has 3 peaks.

6.8 Initial Calibration Verification Standard Solutions (ICV)

- 6.8.1 Stock standard solutions prepared from a second source vendor's standards or a different lot from the same vendor as the calibration standards containing all of the analytes listed in Section 8.2, diluted in Hexane.
- 6.8.2 ICV standards are equivalent to Level 3 calibration standard in concentration listed in Section 8, Tables 8.2.2.

6.9 QC Spiking Solution

- 6.9.1 The spiking solution for SW846-8082 samples is typically a mix of PCB 1016 and PCB 1260 (PCB 1660). The typical volumes of standards used for preparing spikes are given in Section 6.9.2. These may be adjusted if necessary to meet the final

concentration if the concentration of the vendor stock changes. An alternate PCB may be used for QC purposes if required for a special project.

- 6.9.2 **PCB 1660 Spike:** The PCB 1660 100XP is made from a 4-8µg/mL SS:Surrogate Stock mix and 200µg/mL PCB 1660 Stock mix in Acetone. The PCBs may be added individually as PCB 1016 and PCB 1260 if necessary or alternate PCBs may be substituted if required. If the initial concentration is different from 200µg/mL, the volumes may be adjusted to meet the final concentration in Table 6.9.2.1. See Tables 6.9.2.1 – 6.9.2.2.

Table 6.9.2.1 – 8082 PCB 1660 100XP Spiking Standard in Acetone

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|---|-------------------------------|--------------|-----------------------------|
| SS:TCMX | 4.0 | 5.0 | 0.40 |
| SS:DCPB | 8.0 | | 0.80 |
| PCB 1660 (1016 + 1260) | 200 | 2.5 | 10 |
| Total Volume of Standard Aliquot | | 7.5mL | |
| Addition of Acetone to Standard Aliquot | | 42.5mL | |
| Final Volume of PCB 1660 100XP Spiking Standard | | 50mL | |

Table 6.9.2.2 – 8082 PCB 1660 10XP Spiking Standard Final Concentration in Hexane

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|--|-------------------------------|--------------|-----------------------------|
| SS:TCMX | 0.40 | 1.0 | 0.04 |
| SS:DCPB | 0.80 | | 0.08 |
| PCB 1660 (1016 + 1260) | 10 | | 1.0 |
| Total Volume of Standard Aliquot | | 1.0mL | |
| Addition of Hexane to Standard Aliquot | | 9.0mL | |
| Final Volume of PCB 1660 10XP Spiking Standard in Sample Extract | | 10mL | |

6.10 Surrogate Spiking Solution

- 6.10.1 The Surrogate Spiking solution is made from a 100-200µg/mL mix in Acetone. Note: Surrogates may be added individually if a mix is not available. Volumes may be

adjusted if necessary to meet final concentration of 4-8µg/mL. The surrogates are spiked at 1.0mL per sample with a sample extract final volume of 10mL.

Table 6.10.1 – 8082 SS: Surrogate Standard Spiking Solution 1000XPSS Standard in Acetone

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|--|-------------------------------|--------------|-----------------------------|
| SS:TCMX | 100 | 2.0 | 4.0 |
| SS:DCBP | 200 | | 8.0 |
| Total Volume of Standard Aliquot | | 2.0mL | |
| Addition of Acetone to Standard Aliquot | | 48mL | |
| Final Volume of SS Spiking Solution in Acetone | | 50mL | |

6.11 MDL Spike

6.11.1 The MDL Spike is made by diluting the PCB 1660 100XP by 1:10 in Acetone. The PCB MDL spike is spiked at 0.5mL per MDL with a 10mL sample extract final volume, see Tables 6.11.1.1 & 6.11.1.2.

Table 6.11.1.1 – 8082 PCB 1660 MDL Spiking Standard in Acetone

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|---|-------------------------------|--------------|-----------------------------|
| SS:TCMX | 0.40 | 1.0 | 0.04 |
| SS:DCPB | 0.80 | | 0.08 |
| PCB 1660 (1016 + 1260) | 10 | | 1.0 |
| Total Volume of Standard Aliquot | | 1.0mL | |
| Addition of Acetone to Standard Aliquot | | 9.0mL | |
| Final Volume of PCB 1660 MDL Spiking Standard | | 10mL | |

Table 6.11.1.2 – 8082 PCB 1660 MDL Spiking Standard Final Concentration in Hexane

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|--|-------------------------------|--------------|-----------------------------|
| SS:TCMX | 0.04 | 0.50 | 0.002 |
| SS:DCPB | 0.08 | | 0.004 |
| PCB 1660 (1016 + 1260) | 1.0 | | 0.05 |
| Total Volume of Standard Aliquot | | 0.50mL | |
| Addition of Hexane to Standard Aliquot | | 9.5mL | |
| Final Volume of PCB 1660 MDL Spiking Standard in Extract | | 10mL | |

6.12 Expiration Dates

- 6.12.1 All standards that are made for SW846-8082 analysis have an expiration date of six months from the opening of the vendor stock ampule or the manufacturer's expiration date if less than six months from opening.

7 **Sample Collection**

- 7.1 Aqueous samples for Method SW846-8082 are collected in two to four amber, pre-certified 1000mL glass bottles with Teflon lined screw caps.
- 7.2 Samples are cooled to 0-6°C (not frozen) after sample collection. Samples must be extracted within 7 days from collection and analyzed within 40 days of extraction.

8 **Calibration**

8.1 Calibration Curve

- 8.1.1 A five-point calibration is performed for PCB 1016 and PCB 1260 in a PCB 1660 mix. Five-point calibrations for alternate PCBs are performed only if necessary. The calibration system uses traceable certified standards. The calibration is an external standard calibration with an average of response factor linear curve fit and should result in a percent relative standard deviation < 20% between calibration levels of each analyte. The origin may not be forced.

8.2 Calibration Standards

- 8.2.1 All PCB calibration curves consist of calibration standards at the following concentrations (µg/mL): The PCB 1660 curve will be used as reference. All other PCBs (1221, 1232, 1242, 1248, 1254, 1262 & 1268) will be made in the same way unless the vendor stock is different than 200µg/mL and will have the same concentration levels as PCB 1660 in Table 8.2.2. Volumes may be adjusted to meet the final concentrations in Table 8.2.2. The PCB 1660 calibration curve is made from

a 4000-8000µg/mL SS: Surrogate Stock mix and 200µg/mL PCB 1660 Stock.

Table 8.2.1 – 8082 PCB 1660 200XP Calibration Stock Standard in Hexane

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|---|-------------------------------|--------------|-----------------------------|
| SS:TCMX | 4000 | 5.0 | 800 |
| SS:DCPB | 8000 | | 1600 |
| PCB 1660 (1016 + 1260) | 200 | 2.5 | 20 |
| Total Volume of Standard Aliquot | | 7.5mL | |
| Addition of Hexane to Standard Aliquot | | 17.5mL | |
| Final Volume of PCB 1660 200XP Stock Standard | | 25mL | |

Table 8.2.2 PCB 1660 Calibration Curve Levels (µg/mL)

| Compound | Level 1 1XP | Level 2 5XP | Level 3 10XP | Level 4 15XP | Level 5 20XP |
|------------------------|----------------|----------------|-----------------|-----------------|-----------------|
| SS:TCMX | 0.002 | 0.02 | 0.04 | 0.06 | 0.08 |
| SS:DCBP | 0.004 | 0.04 | 0.08 | 0.12 | 0.16 |
| PCB 1660 (1016 + 1260) | 0.05 | 0.50 | 1.0 | 1.5 | 2.0 |

Table 8.2.3 Aliquots of PCB 1660 Calibration Stock to make up all the levels in Table 8.2.2

(Aliquots corresponds to each level directly above each column)

| | Level 1 1XP | Level 2 5XP | Level 3 10XP | Level 4 15XP | Level 5 20XP |
|--|-------------------|-------------------|-------------------|-------------------|-------------------|
| Aliquot of PCB 1660 Calibration Stock 200XP (see Table 8.2.1) | 0.050mL (50µL) | 0.25mL (250µL) | 0.50mL (500µL) | 0.75mL (750µL) | 1.0mL (1000µL) |

Note: Bring all levels (points of the curve) up to 10mL by using **Hexane**

8.3 Calibration Verification

8.3.1 Second source calibration verification (ICV) must be analyzed after each initial calibration. All analytes must be within $\pm 15\%$ of the expected value.

8.3.2 The ICVs for all PCBs are equivalent in concentration to Level 3 of the calibration curves.

- 8.3.3 The PCB 1660 ICV is made from individual PCB 1016 and PCB 1260 100µg/mL PCB Stocks. If the ICV vender stock is the same concentration as the Primary standard, then the ICV is made exactly like the primary calibration curve at Level 3 in Section 8.2. Surrogates are not included. All other PCBs (1221, 1232, 1242, 1248, 1254, 1262 and 1268) will be made in the same way unless the vendor stock is different than 100µg/mL.

Table 8.3.3.1 – 8082 PCB 1660 ICV 100XP-ICV Stock Standard in Hexane

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|---|-------------------------------|--------------|-----------------------------|
| PCB 1016 | 100 | 1.0 | 10 |
| PCB 1260 | 100 | 1.0 | 10 |
| Total Volume of Standard Aliquot | | | 2.0mL |
| Addition of Hexane to Standard Aliquot | | | 8.0mL |
| Final Volume of PCB 1660 ICV 100XP-ICV Stock Standard | | | 10mL |

Table 8.3.3.2 – 8082 PCB 1660 ICV 10XP-ICV Stock Standard in Hexane

| Compound | Initial Concentration (µg/mL) | Aliquot (mL) | Final Concentration (µg/mL) |
|--|-------------------------------|--------------|-----------------------------|
| PCB 1016 | 10 | 1.0 | 1.0 |
| PCB 1260 | 10 | | 1.0 |
| Total Volume of Standard Aliquot | | | 1.0mL |
| Addition of Hexane to Standard Aliquot | | | 9.0mL |
| Final Volume of PCB 1660 ICV 10XP-ICV Standard | | | 10mL |

8.4 Record Keeping

- 8.4.1 Documentation of an instrument calibration is reviewed for adherence to quality criteria and archived with project records.
- 8.5 Daily Calibration Verification and Continuing Calibration
- 8.5.1 A continuing calibration standard (CCC) ensures the instruments target compound retention times and quantitation parameters meet method performance criteria. For any 12-hour analysis period, prior to sample analysis, a mid-point daily continuing calibration verification is performed for each pesticide and multi-component mix. Continuing calibration standards are analyzed during the analysis period to verify that instrument calibration accuracy does not exceed $\pm 15\%$ of the initial calibration, i.e. $\% \text{Drift} \leq 15\%$ (calculation 11.7). If the continuing calibration does not meet method performance criteria, then the instrument must be re-calibrated. A CCC is required after running the standard curve and initial calibration verification. After performing an initial calibration, an ICV may be substituted for a CCC if it meets method criteria for a CCC.
- 8.6 Average Response Factor Calibration
- 8.6.1 To evaluate the linearity of the initial calibration, calculate the mean response factor (RF), the standard deviation (σ_{n-1}) and the relative standard deviation expressed as a percentage (%RSD). If the %RSD of the response factors is $\leq 20\%$ over the calibration range, then linearity through the origin may be assumed, and the average calibration or response may be used to determine sample concentrations. See Calculations 11.2.
- 8.7 Linear Calibration using First Order Least Squares Regression
- 8.7.1 Linearity through the origin is not assumed in a least squares fit. The instrument responses versus the concentration of the standards for the 5 points are evaluated using the instrument data analysis software. The regression will produce the slope and intercept terms for a linear equation. The regression calculation will regenerate a correlation, r , a measure of goodness of fit of the regression line to the data. A value of 1.0 is a perfect fit. An acceptable correlation of coefficient should be $r \geq 0.990$ (or $r^2 \geq 0.980$). See Calculations 11.4.
- 8.7.2 Alternatively, second order quadratic fit may be used with an acceptable correlation of coefficient of $r \geq 0.990$ (or $r^2 \geq 0.980$). Note: quadratic fit will be calculated by chromatographic software. See Calculation 11.5.
- 8.8 Retention Time Windows
- 8.8.1 The width of the retention time window for each analyte, surrogate and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time of CCCs established over a 72 hour period from beginning injection to final injection over four days, with final injection occurring at a time earlier than the first injection so as to not exceed 72 hours. See Calculation 11.6.
- 8.8.2 CCCs used for RT Studies only are not required to meet continuing calibration criteria.

8.9 Daily Retention Time Update

8.9.1 Retention Times (RT) are updated once every 12 hours when ran on a GC for 8082 analysis. Each CCC is processed using Totalchrom software and the subsequent new RTs are saved in a copy of the Totalchrom method used for analyzing this batch of samples. To the existing Totalchrom method an extension is added by using "Month-Day-Year." The vial number where the update occurred may also be added to prevent confusion as there may be up to three or more RT updates in a single sequence. Hard copies of the calibration parameters are included with the data package for that batch of samples.

8.10 Verification of Linear Calibrations

8.10.1 Calibration verification for linear calibrations involves the calculations of % drift of the instrument response between the initial calibration and each subsequent analysis of the verification standard. The % drift may be no more than $\pm 15\%$. See Calculation 11.7.

8.11 Sample Concentration

8.11.1 Sample results are expressed in $\mu\text{g/L}$. See Calculation 11.9.

8.11.2 If an analyte response is calibrated by Average Response Factor, \overline{RF} , the chromatographic software calculates the concentration of the extract per equation 11.8, Calculations in $\mu\text{g/mL}$.

8.11.3 If an analyte response is calibrated by linear regression, the chromatographic software calculates the concentration of the extract solving for x per equation 11.4, Calculations in $\mu\text{g/mL}$.

8.11.4 If an initial volume of other than 1000mL is used or a dilution of the extract is analyzed, the final sample result is multiplied by the factor determined per equation 11.10.

9 **Quality Control**

9.1 Refer to Table 14.1 for Reporting Limits (RLs), Appendix A, Table A.1 for Quality Assurance criteria and Table 14.2 for a summary of Quality Control procedures associated with this method.

9.2 A Method Detection Limit Study for all analytes must be performed once per year. Refer to SOP Reference 13.4.

9.2.1 A Method Detection Limit study for all analytes must be performed initially, after major instrument repairs or changes to extraction procedures. MDL studies performed for these purposes can be done by the extraction and analysis of 7 samples and 7 blanks over 3 separate days.

9.2.2 The 7 MDL sample study is performed by extracting 7 spiked MDL samples, $\text{MDL}_{\text{Spike}}$, spiked at the lowest point of the curve and extracted along with 7 blank MDL samples, $\text{MDL}_{\text{Blank}}$. These sets of spiked and blank samples are extracted over 3 separate days and analyzed over a period of 3 separate days. There is a non-analysis

day between each of the 3 days. A total of 14 samples are extracted, 7 spiked and 7 blank.

- 9.2.3 **On a continuous basis**, MDLs are performed by extraction and analysis of one sample spiked as an MDL_{Spike}, at the lowest point of the curve and extracted with every batch of samples along with the method blank, MDL_{Blank}, per each batch of samples. The results of the MDL_{Spike} and MDL_{Blank} will be entered into LabWorks using the blank test code \$B_8082H, and the MDL test code, \$ML8082H, and the MDL Spiked Amount, \$MA8082H. MDL reports will be pulled from LabWorks at a minimum of once per year (See SOP reference 13.4).
- 9.2.4 The higher value of the 2 MDLs, MDL_{Blank} or MDL_{Spike} will be used as the reporting MDL.
- 9.3 Refer to SOP Reference 13.1 for training and certification procedures.
- 9.4 Refer to SOP Reference 13.2 for control charting procedures.
- 9.5 LCS control limits are used to monitor LCSD recovery. LCSD recovery is not used to validate batch data; however, the LCS/LCSD precision (%RPD) is used for batch validation.
- 9.6 MS/MSD pairs are analyzed at a minimum of 5% of all samples analyzed.
- 9.7 Control Limits
- 9.7.1 Note: Analysts must use the control limits presented in Appendix A, Table A.1 for LCS/LCSDs. Those limits cannot exceed the default limits presented in Table 9.7.1.

Table 9.7.1: Default QC Limits*

| | Compound | Default LCL %Recovery | Default UCL %Recovery | Default Precision %RPD |
|------------------|------------------|--------------------------|--------------------------|------------------------------|
| LCS/LCSD | | | | |
| | PCB 1016 | 10 | 200 | 30 |
| | PCB 1221 | 10 | 200 | 30 |
| | PCB 1232 | 10 | 200 | 30 |
| | PCB 1242 | 10 | 200 | 30 |
| | PCB 1248 | 10 | 200 | 30 |
| | PCB 1254 | 10 | 200 | 30 |
| | PCB 1260 | 10 | 200 | 30 |
| | PCB 1262 | 10 | 200 | 30 |
| | PCB 1268 | 10 | 200 | 30 |
| Surrogate | | | | |
| | TCMX (Surrogate) | 10 (0.04µg/L) | 200 (0.80µg/L) | NA |
| | DCBP (Surrogate) | 10 (0.08µg/L) | 200 (1.6µg/L) | NA |

Table 9.7.1: Default QC Limits*

| | Compound | Default LCL %Recovery | Default UCL %Recovery | Default Precision %RPD |
|---------------|-------------------|----------------------------------|----------------------------------|---------------------------------------|
| MS/MSD | Same as LCS/LCSD* | | | |

*Methods 8000B and 8082 do not specify a range limit for Surrogate, LCS or MS recoveries or precisions. LCS recoveries are derived from Control Charting. The EPD lab will use the LCS/LCSD limits for the MS/MSD recovery limits. No recovery may be less than 10% or higher than 200%. The EPD Lab sets a default of no higher than 70% for the LCL and no less than 130% for the UCL. Precision RPD will be set at 30% default.

9.8. Method Detection Limit Study (MDL):

- 9.8.1. MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.
- 9.8.2. The actual MDL varies depending on instrument and matrix.
- 9.8.3. The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.
- 9.8.4. An MDL study may be done two different ways. The two different ways are considered and initial MDL study and a continuous MDL study. Both ways will be explained below.

9.9. Initial MDL study:

- 9.9.1. An initial MDL study may occur when a new instrument is brought online, changes to the method (which affect the compound of interest's peak area), and lastly major instrument repairs have been made.
- 9.9.2. An initial MDL study will consist of the following operating parameters, 7 MDL samples and 7 MDL blanks. The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blanks.

9.10. Continuous MDL study:

- 9.10.1. A Continuous MDL study is preferred over the initial except in a few cases. For a continuous MDL study to be used on an instrument it must have a minimum of 7 MDL samples and 7 MDL blanks extracted over the course of multiple batches over a year. It is required that at a minimum 2 MDL samples and 2 MDL blanks must be ran per quarter per instrument. If this requirement is not met, then the initial MDL study must be performed for that instrument. (See section 9.9.2 for requirements.)
- 9.10.2. A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.
- 9.10.3. The results of the MDLBlank will be entered into Labworks using the Method Blank

test code, \$B_8082H. The MDLSpike result will be entered using the \$ML8082H. The MDL Spiked Amount will be entered into the test code \$MA8082H. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-8082H.

- 9.10.4. MDL studies must be pulled on a yearly basis or an initial MDL study must be performed before the current MDLs for the instrument expire.

10 Procedure

- 10.1 Refer to GA EPD Laboratory SOP – Separatory Funnel Liquid-Liquid Extraction – EPA Method 3510C, SOP 1-028, Rev. 7 or later for the sample prep and extraction procedure.
- 10.2 Upon completion of the extraction procedure, samples are diluted if necessary and vialled in 2mL autosampler vials using 300µL inserts to preserve sample volume if desired.
- 10.3 Analyze all sample extracts and QC using a gas chromatograph equipped with an electron capture detector.
- 10.4 Sample response is measured against the calibration curves. If the response exceeds the upper limit of the curve, the sample extract is diluted and re-analyzed.
- 10.4.1 Dilutions: Upon analysis of the extract, if a target compound response is greater than that of the highest standard of the calibration curve, the sample must be diluted with the final extraction solvent (Hexane) so that, upon analyzing the dilution (in a valid analysis sequence), the target response is between the lowest concentration standard (or the reporting limit, whichever is higher) and the highest concentration standard.
- 10.5 A detect is considered to be positive if the quantitation amount is greater than the Reporting Limit for that compound. When a positive detect is found, the sample must be re-analyzed on a second, dissimilar confirmation column. If the difference between the quantitation amount found for the detected compound on the primary column and the confirmation column is greater than 40%, the detected compound is considered to be not confirmed. The Blanks, LCS and MS values are taken from the primary column. If the results of this column are out of acceptable range due to matrix interferences or other problems, the results may be reported from the confirmation column provided the calibration criteria are met.
- 10.5.1 If a detect for a PCB other than PCB 1660 occurs, the instrument will be calibrated with a five point curve for the alternate PCB and the Blank and affected sample(s) will be reanalyzed against this curve for concentration, retention time and pattern match.
- 10.6 For all PCB mixes, a fingerprint pattern and retention time match is required.
- 10.6.1 The chosen peaks for each PCB mix should not be disproportionately larger or smaller in the sample compared to the standard. The areas of the four (or more) peaks should be summed and averaged for use in determining the PCB concentration.

11 Calculations

11.1 Response Factor, RF, for a peak

$$RF = \frac{\text{Area}_{\text{Analyte}}}{\text{Concentration}_{\text{Analyte}}}$$

11.1.1 Where:

RF = Response Factor

Area_{Analyte} = Area of the peak of the analyte of interest

Concentration_{Analyte} = Concentration of the analyte of interest in µg/ml

11.2 Average Response Factor, \overline{RF}

$$\overline{RF} = \sum \frac{RF_i}{n}$$

11.2.1 Where:

\overline{RF} = Mean response factor

RF_i = Response factor of compound at each level i

n = Number of calibration standards

11.3 Sample Standard Deviation ($n - 1$) (σ_{n-1}) of response factors

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^n \frac{(RF_i - \overline{RF})^2}{n-1}}$$

11.3.1 Where:

σ_{n-1} = Sample Standard Deviation

\overline{RF} = Mean response factor

RF_i = Response factor of compound at each level i

n = Number of calibration standards

11.4 First Order Linear Regression Response Equation

$$Y = ax + b$$

This rearranges to:

$$x = Y - b/a$$

11.4.1 Where:

Y = Instrument response

a = Slope of the line

b = Intercept

x = Concentration in the extract or standard

11.5 Second Order Quadratic Fit Equation

11.5.1 $Y = ax^2 + bx + c$

11.5.2 Where:

Y = Instrument response

a = Slope of the line

b = Intercept

c = constant

x = Concentration in the extract or standard

11.5.3 Subtract Y from c to get modified equation $0 = ax^2 + bx + c$

11.5.4 Solve for x using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

11.5.5 A positive and negative value will be generated. Use positive value.

11.6 Average Retention Time, \overline{RT}

$$\overline{RT} = \sum \frac{RT}{n}$$

11.6.1 Where:

\overline{RT} = Mean retention time for the target compound

RT = Retention time for the target compound

n = Number of values

11.7 Percent Drift, %Drift

$$\%Drift = \frac{(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}})}{\text{Concentration}_{\text{Expected}}} * 100$$

- 11.7.1 Where:
Concentration_{Calculated} = Concentration calculated from result
Concentration_{Expected} = Theoretical concentration of the standard

11.8 Extract Concentration Calculation (µg/mL)

$$\mu\text{g}/\text{mL} = \frac{(A_s)}{(\overline{\text{RF}})}$$

- 11.8.1 Where:
 A_s = Peak area of analyte
 $\overline{\text{RF}}$ = Average Response Factor

11.9 Sample Concentration Calculation (µg/L)

$$\mu\text{g}/\text{L} = \frac{(A_s)(V_t)(D)}{(\text{RF})(V_i)(V_s)}$$

- 11.9.1 Where:
 A_s = Area of peak for analyte in sample
 V_t = Extract volume in mL
 D = Dilution factor
 RF = Mean response factor (area per µg)
 V_i = Volume of sample injected in µL
 V_s = Original sample volume in mL

11.10 Sample Concentration Adjustment for Varying Initial Volume and Dilutions

$$\mu\text{g}/L_{\text{Corrected}} = \mu\text{g}/L_{\text{Uncorrected}} * \frac{(1000 \text{ mL})(\text{DF})}{V_s}$$

- 11.10.1 Where:
 DF = Dilution Factor
 V_s = Original sample volume in mL

11.11 Quality Control Calculations

$$\text{LCS/LCSD/ICV \% Recovery} = \frac{R_{\text{spike}}}{\text{Expected Result}} \times 100$$

$$\% \text{ RPD(precision)} = \frac{\left| \frac{R_{\text{sample}} - R_{\text{duplicate}}}{\frac{R_{\text{sample}} + R_{\text{duplicate}}}{2}} \right|}{\left(\frac{R_{\text{sample}} + R_{\text{duplicate}}}{2} \right)} \times 100$$

11.11.1 Where:

R_{spike} = % recovery of spiked sample

R_{sample} = % recovery of sample

$R_{\text{duplicate}}$ = % recovery of duplicate sample

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP6-015, online revision.

13 References

13.1 GA EPD Laboratory SOP's- Initial Demonstration of Capability SOP 6-001, online revision or later and/or Continuing Demonstration of Capability SOP 6-002, online revision.

13.2 GA EPD Laboratory SOP- EPD Laboratory Procedures for Control Charting and Control and Control Limits SOP, SOP 6-025, online revision.

13.3 GA EPD Laboratory SOP- EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.4 GA EPD Laboratory SOP- Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.5 GA EPD Laboratory SOP 1-052, Organics Data Validation, online revision.

13.6 GA EPD Laboratory SOP – Separatory Funnel Liquid-Liquid Extraction – EPA Method 3510C, SOP 1-028, online revision.

13.7 GA EPD Laboratory Chemical Hygiene Plan, online revision.

13.8 EPA Method SW846-8000B – Determinative Chromatographic Separation, online revision.

13.9 EPA Method SW846-8082 – Polychlorinated Biphenyls (PCBs) By Gas Chromatography, Rev. 0, December 1996.

13.10 EPA Method SW846-3510C – Separatory Funnel Liquid-Liquid Extraction, Rev. 3, December 1996.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

14.1 Refer to Appendix A, Table A.1 for precision and accuracy criteria.

Table 14.1 RLs for EPA Method SW846-8082 in Water

| Parameter/Method | Analyte | Matrix (Water) | |
|--------------------|----------|----------------|------|
| | | RL | Unit |
| SW846-8082 (Water) | PCB 1016 | 1.0 | µg/L |
| | PCB 1221 | 1.0 | µg/L |
| | PCB 1232 | 1.0 | µg/L |
| | PCB 1242 | 1.0 | µg/L |
| | PCB 1248 | 1.0 | µg/L |
| | PCB 1254 | 1.0 | µg/L |
| | PCB 1260 | 1.0 | µg/L |
| | PCB 1262 | 1.0 | µg/L |
| | PCB 1268 | 1.0 | µg/L |

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8082 in Water

| Method | Applicable Parameter | QC Check | Minimum Frequency | Acceptance Criteria | Corrective Action | Flagging Criteria |
|-------------------------------|----------------------------------|--|--|--|---|-------------------|
| EPA Method SW846-8082 (Water) | Polychlorinated Biphenyls (PCBs) | 5-point initial calibration for all analytes | Initial calibration prior to sample analysis | RSD for all analytes $\leq 20\%$ linear-least squares regression $r \geq 0.990$ or $r^2 \geq 0.980$ | Correct problem then repeat initial calibration | |

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8082 in Water

| Method | Applicable Parameter | QC Check | Minimum Frequency | Acceptance Criteria | Corrective Action | Flagging Criteria |
|-------------------------------|----------------------------------|--|--|---|---|-------------------|
| EPA Method SW846-8082 (Water) | Polychlorinated Biphenyls (PCBs) | Initial calibration verification (CCC) | Beginning each analysis sequence prior to the analysis of samples, after every 12 hours, and at the end of the analysis sequence | All analytes within $\pm 15\%$ of expected values | If out of range high, high bias with no detects, generate a corrective action and use data. If low bias or with detects, rerun CCC and affected samples. If rerun passes, use data. If reruns do not pass, correct problem, repeat initial calibration verification and re-analyze all samples since last successful calibration verification | |
| | | Second source calibration verification (ICV) | Once per initial calibration | All analytes within $\pm 15\%$ of expected value | Correct problem then repeat initial calibration | |
| | | Retention Time window calculated for each analyte | Once per year or after major maintenance that would affect RTs | ± 3 times standard deviation for each analyte retention time for standard analytical batch sequence | Correct problem then re-analyze all samples analyzed since the last retention time check | |
| | | Retention time window update | Must be done every 12 hours with each CCC and prior to sample analysis | First CCC of each sequence and then every 12 hours | None | |
| | | IDC- Demonstrate ability to generate acceptable accuracy and precision using four replicate analyzes of a QC check sample, a Blind and a Blank | Once per analyst | QC acceptance criteria Table A.1, Appendix A | Locate and fix problem then re-run or re-extract demonstration for those analytes that did not meet criteria | |

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8082 in Water

| Method | Applicable Parameter | QC Check | Minimum Frequency | Acceptance Criteria | Corrective Action | Flagging Criteria |
|-------------------------------|----------------------------------|-------------------------------|--|---|--|---|
| EPA Method SW846-8082 (Water) | Polychlorinated Biphenyls (PCBs) | Surrogate spike | Every sample, spiked sample, standard and method blank | QC acceptance criteria Table A.1, Appendix A | Analyze second extract aliquot, if this does not pass, correct problem then re-extract and re-analyze the sample | |
| | | Method Blank Solvent Blank | One per analytical batch of 20 or less samples | No analytes detected >RL | Analyze second extract aliquot, if this does not pass, correct problem then re-analyze or re-extract the blank and all samples in the affected batch | |
| | | LCS/LCSD for all analytes | One per analytical batch of 20 or less samples | QC acceptance criteria Table A.1, Appendix A | Reanalyze once. If they fail a second time, correct problem the reanalyze or re-extract the LCS/LCSD and all samples in the affected batch | Flag QC sample report if LCSD exceeds upper acceptable control limits with passing RPD when high bias with no detects |
| | | MS/MSD | Minimum of 5% of all samples analyzed | QC acceptance criteria Table A.1, Appendix A | Flag QC sample report | |
| | | Second-column confirmation | 100% for all positive results, ≤ 40% RPD for confirmation | If used for quantitation, same as for initial or primary column analysis | Same as for initial or primary column analysis | |
| | | MDL study | Once per year or after major maintenance of the instrument | All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1 | Re-do MDL Study | None |

Table 14.2 Summary of Calibration and QC Procedures for EPA Method SW846-8082 in Water

| Method | Applicable Parameter | QC Check | Minimum Frequency | Acceptance Criteria | Corrective Action | Flagging Criteria |
|--------|----------------------|-------------------------------------|---|---|--|-------------------|
| | | MDL analysis | Once per batch or as needed to acquire data points per SOP 6-007, online revision | All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria | Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data | None |
| | | Results reported between MDL and RL | None | None | None | |

15 Associated LabWorks Test Codes**15.1 Parent Test Code**

15.1.1 \$8082H

15.2 Extraction Test Code

15.2.1 EXTN_P

15.3 QC Test Codes

15.3.1 \$B_8082H – Extraction Blank Results

15.3.2 \$LA8082H – LCS/LCSD Spike Amount

15.3.3 \$LS8082H – LCS Results

15.3.4 \$LD8082H – LCSD Results

15.3.5 \$LR8082H – LCS Percent Recovery

15.3.6 \$L28082H – LCSD Percent Recovery

15.3.7 \$LP8081H – LCS/LCSD Precision

15.3.8 \$A_8082H – MS/MSD Spike Amount

15.3.9 \$S_8082H – MS Results

15.3.10 \$D_8082H – MSD Results

15.3.11 \$R_8082H – MS Percent Recovery

15.3.12 \$RD8082H – MSD Percent Recovery

15.3.13 \$P_8082H – MS/MSD Precision

15.3.14 \$MA8082H – MDL Spike Amount

15.3.15 \$ML8082H – MDL Results

Appendix A – Quality Assurance Criteria for EPA Method SW846-8082 in Water

| Table A.1 | | | | |
|-------------|------------------------|---------------|---------|------------------|
| QC Type | Analyte | Accuracy (%R) | | Precision (%RPD) |
| | | LCL | UCL | |
| LCS/LCSD* | PCB 1016 | 63 | - 139 | 30 |
| | PCB 1221 | 50 | - 150 | 30 |
| | PCB 1232 | 50 | - 150 | 30 |
| | PCB 1242 | 50 | - 150 | 30 |
| | PCB 1248 | 50 | - 150 | 30 |
| | PCB 1254 | 50 | - 150 | 30 |
| | PCB 1260 | 57 | - 146 | 30 |
| | PCB 1262 | 50 | - 150 | 30 |
| | PCB 1268 | 50 | - 150 | 30 |
| Surrogate** | TCMX | 23.5 | - 162 | NA |
| | TCMX (as ug/L) | 0.0940 | - 0.650 | NA |
| | DCBP | 15.0 | - 146 | NA |
| | DCBP (as µg/L) | 0.0120 | - 1.17 | NA |
| MS/MSD*** | Same as LCS Recoveries | See Above | | 30 |

*LCS/LCSD recovery based on Control Charts of data collected from 12/31/2010 to 1/01/2021. The EPD lab typically uses PCB Mix of 1016 and 1260 (PCB1660) for QC. Should any other PCB be used for QC, the EPD lab will default to 50-150% recovery for those compounds. The EPD lab sets a default of 30% RPD for all compounds.

** Surrogate recoveries based on Control Charts of data collected from 12/31/2010 to 1/01/2021.

*** The EPD lab sets the MS/MSD recoveries and precisions as the same as the LCS/LCSDs.

Updates: Appendix A added. Updated to online revision.