PCB Air Sampling Plan for Phase 1 IPWP

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PCB Air Sampling

Background / Purpose of Air Sampling

The overall plan for the project has been designed to control and prevent any emission of blast media or PCB bulk product waste during activities from exiting the controlled work environment by using engineering and administrative controls. In short, it is expected that there will be no airborne emissions from the containment.

Air sampling is part of the inspection and monitoring program to assure the project is protective of human health and the environment. In other words, it is to provide assurance that controls and prevention actions that are put in place are of best practice, are maintained and continue to be acceptable.

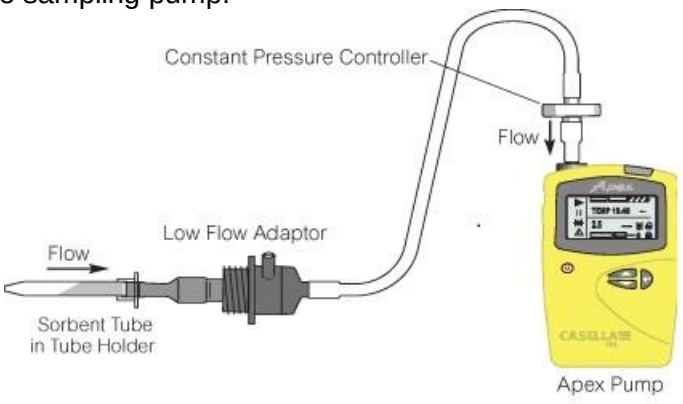
The air testing strategy to take air samples that are analyzed for PCBs and confirming levels are minimally below the NIOSH REL both inside the occupied building undergoing abatement on the exterior and at the HEPA exhaust locations for the negative air machines.

The sampling method of collecting and analyzing air samples for PCBs is specific to the concern of unintentional release of PCB containing material to either the environment inside the occupied building or from air blowing to the outside environment through the HEPA filers on the negative air machine used to maintain the pressure of the containment.

Field Testing Equipment

1 – The “Sampler” is a 13-mm glass fiber filter without binders in a Swinnex cassette followed by a glass tube, 7 cm long, 6-mm OD, 4-mm ID containing two sections of 30/48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; urethane foam between sections and behind the backup section. (The tube will be purchased assembled this way) The cassette and tube will be joined with PVC tubing. Note: The “sampler” will be assembled at NVL Labs.
2 – Sampling pump capable of sampling 1.0 liter per minute with flexible connecting tubing.
3 – Calibrated rotometer

Picture of the sampling pump:



Activity in the Field

1. Information is to be collected on the field data sheet and Chain of Custody (COC) form.
2. All pumps will be calibrated for airflow prior to each and every use with a representative sampler in line.
3. Air flow will be measured using a calibrated rotometer
4. Air flow will typically be at 1.0 liter per minute. (per the method, with anticipation of no to very low levels of airborne PCBs)
5. The actual sampler will be connected to the calibrated pump. This involves per the method:
   -Immediately before sampling, breaking the ends of the Florisil tube and connecting it to the Swinnex cassette.
   -The sampler is then connected to the pump using flexible tubing.
6. Each sample collected, a unique sample number will be generated, which will be put on a label on the sampler and recorded on the field forms. The standard method to generate a unique number will be the date – followed by PCBAIR and then a number. For example, 060814-PCBAIR-1.
7. The sample train is then placed at sample location, with start and end times noted.
8. Samples are collected during the duration of the daily work period, which is anticipated to be between 6 to 8 hours per day.
9. When samples are collected, the pump will be turned off, the time will be noted and the sampler removed.
10. The sampler will then be capped at the Florisil tube end.
11. The sampler will then be placed under refrigeration (typically an ice chest) for transportation.
12. The air flow for the pump will be re-measured and recorded using a representative sampler in line.
13. The sampler will be delivered that day to NVL Labs.

Sample Locations and Volume

Air testing will include the collection of one air sample inside the building adjacent to the area where PCB's containing paint removal is taking place. Air testing will also include the collection of sample outside the containment at locations where air is exhausted from the negative air machine after passing through a HEPA filter. Air sampling inside/outside will be taken for first three days of blasting, followed by reducing the samples to every other day of blasting work (if lab results are below the NIOSH REL), thereafter.

Field QA/QC

Representative field blank samplers will be added periodically. Per the method, 2 to 10 field blank samplers are to be collected per set. For the purpose of document, a set will be considered the samples collected for an IPWP.

A field blank sampler is treated exactly like a sample, except that no air is drawn through the sampler.

At the Laboratory

All samples will be extracted within 1 week after collection. All samples will be stored at <4 degrees Celsius until extracted. At this moment, the planned turnaround time for analysis will be between 1 to 5 business days.

Laboratory Analysis Method

Method based on NIOSH Method 5503.

Equipment

- **Sampler:** 13-mm glass fiber filter without binders in a Swinnex cassette (Cat. No. SX 0001300, Millipore Corp.) followed by a glass tube, 7 cm long, 6-mm OD, 4-mm ID containing two sections of 30/48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; urethane foam between sections and behind the backup section. (SKC 226-39, Supelco ORBO-60, or equivalent) Join the cassette and Florisil tube with PVC tubing, 3/8" L x 9/32" OD x 5/32" ID, on the outlet of the cassette and with another piece of PVC tubing, 3/4" L x 5/16" OD x 3/16" ID, complete the union.
- Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
- Tweezers.
- Vials, glass, 4- and 7-mL, with aluminum or PTFE-lined caps
- Volumetric flasks, 10-mL and other convenient sizes for preparing standards.
- Gas Chromatograph equipped with split/splitless inj. dual column and ECD detectors (Shimadzu GC-2010 Plus)
- Columns:
  ZB-Multiresidue-1, serial# 207631 (30m., 0.32mmID, 0.50um df),
  ZB-Multiresidue-2, serial# 278651 (30m., 0.32mmID, 0.25um df).
- Detectors: Shimadzu Electron Capture Detector (2)
- Auto Sampler.
- Fume hood.
- Centrifuge.
- Shimadzu GC Real Time Analysis (Acquisition and analysis software).
- Analytical balance capable of accurately weighing to at least +/-0.001.
- Vortex
- Hot Plate

Reagents and Supplies

- Hexane, pesticide quality.

- Florisil, 30/48 mesh sieved from 30/60 mesh. After sieving dry at 105 °C for 45 min. Mix the cooled Florisil with 3% (w/w) distilled water.
- Nitrogen, purified.
- Stock standards of all nine Aroclors at 1000 ppm in methanol or isooctane from Absolute.
- Standards for calibration and pattern recognition.
- Second source standards for Aroclors 1016, 1260 and 1254 from Supelco at 1000 ppm.
- Calibration standards: mixture of AR1016 and AR1260 at a concentration from 0.02, 0.05, 0.1, 0.2 and 0.5 ppm for external standard calibration.
- Glass centrifuge tubes with caps.
- Amber autosampler vials.
- Glass pipettes.
- Gas-Tight syringes: 10ul, 100 ul and 500 ul.
- Filter paper: 9.0 cm.
- Razor Blades (for chopping)/scissors.
- Mortar and Pestle (for grinding).
- 2,4,5,6-Tetrachloro-M-Xylene (TMX) combined with DCB at a 1:1 ratio, yielding a 10 ppm surrogate mix).
- 250ul glass flat bottom inserts for GC vial.
- Baked Florisil :Resprep: 60/100Mesh, LOT#316050-CB, CAT# 26135
- Sulfuric Acid : JT Baker: CAS # 7664-93-9, Lot# B03032
- Extraction tubes.
- Copper:
- Aluminum pan for drying
- Nitric Acid
- Acetone

Working Standard making procedure (In Hexane – can be prepared in stock and kept in fridge for 6 months)

Standard type	Supplier	Initial concentration	Volume used	Final Volume
100ppm DCB/TMX Surrogate	Absolute	-TMX @1000ppm -DCB @ 1000ppm	500ul of each	5mL
0.1 ppm1016+1260 mix Initial Cal / CCV + 0.1ppm Surrogate	Absolute	-ARC1016 @100ppm -ARC1260@100ppm -100ppm DCB/TMX mix	10ul of each	10mL
0.1ppm ICV	Supelco	-ARC1016 @100ppm -ARC1260@100ppm	10ul of each	10mL
0.02ppm std (1016/1260 mix)	Absolute	-ARC1016 @100ppm -ARC1260@100ppm	2ul of each	10mL
0.05ppm std (1016/1260 mix)	Absolute	-ARC1016 @100ppm -ARC1260@100ppm	5ul of each	10mL
0.10ppm std (1016/1260 mix)	Absolute	-ARC1016 @100ppm -ARC1260@100ppm	10ul of each	10mL
0.20ppm std (1016/1260 mix)	Absolute	-ARC1016 @100ppm -ARC1260@100ppm	20ul of each	10mL
0.50ppm std (1016/1260 mix)	Absolute	-ARC1016 @100ppm -ARC1260@100ppm	50ul of each	10mL
0.1ppm1254 Cal + 0.1ppm Surrogate	Absolute	-100ppm 1254 Aroclor -100ppm DCB/TMX mix	10ul of each	10mL

Note: 0.1ppm of Individual aroclors of PCB can be prepared by adding 10uL of 100ppm of Working Stock standard, plus 10uL of 100ppm DCB/TMX surrogate mix and diluting to 10mL final volume in a volumetric flask.

GC Conditions

- Shimadzu 2010 Plus equipped with AOC-20i Auto-Injector and Shimadzu GC Real Time Analysis (acquisition and analysis software).
- Dual-column analysis with ZB-Multiresidue-1, serial# 207631 (30m., 0.32mmID, 0.50um df), and ZB-Multiresidue-2, serial# 278651 (30m., 0.32mmID, 0.25um df).
- Single injection with a Restek Siltek, Universal Y Connector to two Shimadzu electron capture detectors (ECD).
- Operating conditions:
- Carrier gas: (He)
- Column flow rate: 3 ml/min
- Make-up gas: (P5)
- Injection volume: 2ul
- Equilibration time: 0.5 min.
- Oven temperature program:
- Initial 150 deg. C, hold 2 min, rate 7 deg/min to 320 deg hold 5 min for a 31.29 min run time.
- Injector: splitless
- Split: N/A
- Purge flow: 2 ml/min
- Temperature: 320 deg C
- Linear velocity: 43.4 cm/sec
- Pressure: 69.6 kPa
- Detectors settings: flash vaporization
- Temperature: 320 deg. C
- Current: 2nA
- Sampling rate: 40 msec
- Filter time constant: 200 ms

Extraction Procedure - Disassembly of the "Sampler": Filter + Solid Sorbent samples. (13-mm glass fiber + Florisil, 100 mg/50 mg)

The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; glass wool between sections and behind the backup section.

1. Place the glass wool and 100-mg Florisil bed in the same 7-mL vial in which the filter was stored. Add 5.0 mL hexane.
2. In a 7-mL vial, place the 50-mg Florisil bed including the two sets of glass wool. Add 2.0mL hexane.
3. Prepare a MB/MS/LCS by placing some of the clean Florisil bed + filter paper in each QC.
4. Add 5mL Hexane to all the QC samples. Add secondary source Aroclor 1016/1260 standard mix to the LCS at 0.1ppm, add secondary source Aroclor 1254 at 0.1ppm to MS.
5. Add 100ppm mixture of TMX/DCB surrogate at 0.1ppm to all client samples plus method QC.
6. Allow to stand for 20 min with occasional agitation.
7. Centrifuge for 10mins
8. Pipette the hexane layer into GC vials for analysis.

PCB Extract Cleanup procedure.

Sulfuric Acid Cleanup:

Sulfuric acid clean up is conducted on PCB extracts whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the Pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

1. Add 1mL Conc Sulfuric Acid to the 2ml PCB extract in the centrifuge tube. Cap the tube and vortex for 60 seconds. Allow for the 2 layers (acid/ Hexane) to separate.
    a. **Caution**: Stop the vortexing immediately if the vial leaks.
    b. AVOID SKIN CONTACT, SULFURIC ACID BURNS.
2. Centrifuge at 3000rpm for 10 mins.
3. Pipette the top Hexane layer into a clean centrifuge tube.
4. If the Hexane extract still appears dark or there is emulsion in the centrifuge tube, carefully pipette the top visible portion into a clean tube, repeat step 1, 2, till the bottom acid layer appears light pinkish or the Hexane extract appears clear.
5. Proceed to Florisil cleanup

Florisil Cleanup

Florisil has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats,oils, and waxes.

1. Bake the Florisil (to dry) at 100 degrees C for 1hr in a beaker, cool and store in a desiccator.
2. Add 1/4 spatula of florisil to the acid cleaned PCB Hexane extract.
3. Vortex for 20 seconds, centrifuge at 3000rpm for 10mins.
4. Transfer the top Hexane layer into the GC vial for Analysis. OR if sediment samples, then proceed to Sulfur cleanup.

Sulfur cleanup (Mostly done on Sediment samples)

Sulfur cleanup is useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest (often an elevated baseline towards the start of the chromatogram). Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorus pesticides. Therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. Copper granules are used to remove sulfur.

First must remove oxides in the copper by treating with dilute nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone and dry. Store in a clean amber vial in a desiccator for 1 year.

1. Add few Copper granules in to the cleanup florisil extract. Vortex for 60 seconds.
2. Centrifuge and transfer to GC vial for PCB analysis.

3. If there is sulfur present, then the Copper and Hexane extract will appear dark grey/black. If such is the case, transfer the hexane layer in to a clean vial and repeat step 1, 2 till the copper remains shiny.

Calibration:

The calibration is performed by the external standard technique. A multipoint curve consisting of 5 concentrations of Aroclor 1016 and Aroclor 1260 mix (1016/1260 mix) is constructed for each column and its respective detector. The concentrations in the calibration span the range of the concentration of Aroclors expected in client samples. DCB/TMX is calibrated at 0.02, 0.05, 0.1, 0.2 and 0.5 ppm. While the Aroclor 1016/1260 mix are also calibrated at five points (0.02, 0.05, 0.1, 0.2 and 0.5 ppm) to check for detector linearity, the other seven Aroclors have only a single-point calibration level of 0.1 ppm. This includes Aroclor(s), 1221, 1232, 1242, 1248 and 1254, 1262, 1268. 4 to 5 congeners that span the retention time scale of the Aroclor are chosen for each Aroclor. Each congener is at least 25% of the height of the highest peak for that particular Aroclor. The calibration model chosen for the 1016/1260 mix is the same model that is applied to the other seven Aroclors. The 1016/1260 mix calibration will have an r value of greater than 99% for all selected congeners and the group calibration. The Relative Standard Deviation (RSD) for this calibration will also be less than 20%. Should the calibration not meet the above specifications, the associated problem(s) will be identified and corrected prior to a recalibration. An Initial Calibration Verification (ICV) at a mid-point concentration (generally 0.1 ppm) is run to verify the validity of the calibration. It is prepared from a 1016/1260 mix made from a secondary source. The **ICVs** response/recovery should be within +**/- 15% of its intended value**.

The calibration factor is determined by the following equation for each characteristic Aroclor peak (specific congener) in the initial calibration standards:

$$CF = \frac{\text{Peak Area(or height) in the Standard}}{\text{Total Mass of the Standard injected (in nanograms)}}$$

Analysis:

Sample extracts are processed with the same parameters as the calibration curve.

A continuing calibration verification standard (CCV) of the 1016/1260 mix is run at the beginning and end of every 12-hour shift, as well as every 12 hours or a maximum of twenty samples. The laboratory may decide to run the CCV every ten samples depending on the color of the extracts to decrease the number of samples requiring reanalysis.

The CFverification of the CCV must not vary more than a +/- 20 percent difference from the mean CF (CFmean) of the calibration curve. The percent deviation is calculated with following formula:

$$\%\text{Difference} = \frac{\text{CFmean - CFverification}}{\text{CFmean}} \times 100$$

After a qualitative identification has been made by comparing the unknown fingerprint to the correct reference, the concentration of a sample is determined by the response in relation to the calibration curve. Samples are initially screened at a 10X dilution to gage the instrument response and are diluted appropriately following the analysis of the screen (i.e. if the extracts look really dark). NVL will make every attempt to analyze samples at the lowest dilution factor possible to ensure the integrity of

the data produced. If a sample exceeds the upper limit of the curve, the sample must be diluted and reanalyzed. The samples which are reported must be analyzed between two valid CCVs.

When a CCV falls out of the 20% limit any sample analyzed after or before must be reanalyzed. An exception is if the CCV is above the acceptance criteria , i.e. >20%, and the PCB aroclor was not detected in the specific samples, then the extract does not have to be reanalyzed , since the verification standard has demonstrated that if the aroclor was present, then it would have been detected. But if the CCV falls more than 20% below the initial calibration, then reinjection is necessary to protect against reporting a false negative result.

Qualitative Identification: The identification of a PCB as an Aroclor is based on the match between absolute retention times and pattern recognition with a reference fingerprint. Each Aroclor is run at 5 ppm to catalog this pattern on each column. The Shimadzu software allows overlay of chromatograms to confirm a specific pattern of congener retention times and response for each Aroclor. If the sample chromatogram has suspected matrix effects one could either run a dilution or run the extract on the GCMS for confirmation.

Quantitative Identification: Once an Aroclor has been qualitatively identified, it is quantitated by direct comparison to its single point calibration of 4-5 characteristic peaks. This is the case for Aroclors: 1016, 1221, 1232, 1242, 1248, 1254,1260,1262,1268. The concentration for a particular Aroclor is determined by averaging the 4-5 concentrations of the 4-5 characteristic peaks against its one-point curve.

If compound identification is precluded due to interferences (e.g., broad, rounded peaks or ill-defined baselines are present). Corrective action must be taken. Further extract cleanup may be needed or rerun the sample on GCMS to identify if the problem is the sample or the GC itself.

Use the calibration standard analyzed during the run to evaluate retention time stability. If retention time shifting is noticed, determine the cause of the problem and fix it.

1242 and 1248 aroclor pattern is very similar to each other and so is the pattern of 1260 with 1262. Careful pattern matching must be done with the individual standards to ensure the correct aroclor is identified and reported. Where interferences prohibit the identification of the correct pattern between either of the aroclor, then the most dominant one can be reported.

Laboratory QA/QC

From each lot of Florisil tubes, at least one tube will be analyzed for quality control.

Calibration and Quality control will be per steps 8, 9 and 10 described in NIOSH method 5503.

Procedures will also include:

Quality control procedures are necessary to monitor and evaluate analyst competency, the extraction procedure and operation of the GC system.

Initial Demonstration of Proficiency (IDOC): The laboratory must demonstrate the ability to perform the method for which he or she will be generating data, by generating data of acceptable accuracy and precision in a clean matrix. The same is true when any new staff is trained or significant changes in instrumentation are made.

A QC reference sample concentrate or Laboratory Control Spike (LCS) will contain PCBs as Aroclors (1016/1260 mix) at a concentration of 0.1 ppm (the midpoint calibration point. In the initial demonstration of capability, the incumbent shall successively extract and run four of these samples for each matrix that will be encountered during analysis.

Include a midpoint calibration standard i.e. a Continuing Calibration Verification (CCV) before and after every batch or 20 samples, whichever is less (or 10 to minimize repeat injections) in every analysis sequence as a calibration check. For the purposes of sample analysis at NVL, the **CCV** will be run at 0.1 ppm. The response factor for the standard should be within **20% of the initial calibration**. If the CCV is out of this acceptance window then corrective action must be performed before any client samples are analyzed.

The laboratory must have procedures for documenting the method performance (precision, accuracy and detection limit). At a minimum and given adequate sample, this includes the analysis of the following QC samples in addition to the CCV and LCS mentioned above: a method blank (MB), a duplicate (DUP), a matrix spike (MS) and a laboratory control sample (LCS) in each analytical batch as well as the addition of surrogates to each field and QC sample. Recoveries for the MB should be below the RL. The **MS and MSD** pair will have recoveries of **40-140%** with a **50% RPD**. The **LCS/LCSD** pair will have recoveries of **40-140%** with a **50% RPD**.

Documenting the effect of the matrix should include the analysis of at least one matrix spike and duplicate sample and/or an MS/MSD pair. Due to often times limited sample volume, the surrogates are used to monitor the matrix of the samples. An LCS/LCSD will be prepared with each batch and/or a MS/MSD pair will be analyzed given adequate sample. The spike should be an Aroclor mixture of 1016/1260 unless the samples in the batch are known to have a specific Aroclor. The LCS/LCSD consists of an aliquot of a clean (control) matrix similar to sample matrix and of the same weight or volume. They are spiked with a secondary source standard containing the same analytes, at the same concentration as the matrix spike (0.1 ppm). When the results of the matrix spike analysis indicate a potential problem due to sample matrix effects, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Surrogates recoveries: The laboratory must evaluate surrogate recovery data from the individual samples versus the surrogate control limits developed by the laboratory. While the control limits are under development, surrogate recoveries will be between **40-140%.**

Method Performance:

The method detection limit (MDL) is performed to verify the instrument sensitivity. A set of 7 or 8 replicates of LCS's spiked at a level one half the reporting limit are analyzed and entered in a spreadsheet to determine the standard deviation of the replicates. The MDL should be performed on any matrix the laboratory may expect to analyze.

Instrument Maintenance:

System Check: If a calibration standard falls out of control limits the laboratory must determine the cause and perform corrective action. The first step is to run a system check with the GC software. The recommended maintenance is performed and recorded in the instrument maintenance log book.

Projected Detection Limit

Per the method, and the field conditions, an 8-hour sample will typically permit a sample volume of 480 liters to be collected, which will allow a detection limit in the range of 0.06 ug/m3. This meets the air level not to be exceeded referenced to in the Plan of 0.001 mg/m3 = 1.0 ug/m3 (NIOSH REL).

REFERENCE:

NIOSH Method 5503: http://www.cdc.gov/niosh/docs/2003-154/pdfs/5503.pdf