QUALITY ASSURANCE PROJECT PLAN

MIDLAND AREA SOIL SAMPLING
MIDLAND, MICHIGAN

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URS Corporation
9400 Amberglen Boulevard
Austin, Texas 78729
(512) 454-4797

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This appendix is a Quality Assurance Project Plan (QAPP) for use in the Midland Area Soils Interim Response Activity Plan Designed to Meet Criteria (Work Plan). The context for the project, the site background, and conceptual model, objectives, sampling plan and implementation strategy are provided in the Work Plan.

This QAPP describes the sampling and analysis requirements and the quality assurance (QA) and quality control (QC) measures that will be taken for samples collected and analyzed under the Work Plan which describes the sample locations, the frequency of sampling, the sampling methods, and the analytes that are to be assayed.

1.1 OBJECTIVES FOR MEASUREMENT

The purpose of a quality assurance/quality control (QA/QC) program is to produce analytical measurement data of known quality that satisfy the project objectives. In regards to measurement data quality, the QA/QC program shall:

- Provide a mechanism for the ongoing control and evaluation of measurement data quality; and
- Provide measures of data quality in terms of accuracy, precision, completeness, representativeness, and comparability to assess whether the data meet the project objectives and can be used for their intended purpose.

The objective of the chemical measurement data is to generate sufficient information to quantify the presence or absence of chemical contamination within the site's media for the purpose of making remedial decisions. To meet this objective, data acquired during the sample collection phase must be defensible to meet this objective. The quality objectives for the chemical measurement data specify the "quality" of the data needed to enable project personnel to make decisions (e.g., a decision to pick one remediation technique over another, etc.). As such, the objectives determine the type and quantity of data needed to make a decision, as well as the measurement objectives (precision, accuracy) for each type of measurement data collected. The objectives for the analytical data will be:

- To collect samples required for remedial decisions;
- To collect and analyze samples under controlled situations using validated methods; and
- To obtain usable and defensible analytical results.

The following sections discuss the steps that will be taken to ensure the validity of the data acquired during the program. The representativeness of the measurement data is a function of the sampling strategy and will be achieved by following the procedures discussed in this section. The quality of the analytical results is a function of the analytical system and will be achieved by using validated methods and the QC system discussed in this section. The basis for assessing precision, accuracy, completeness, representativeness, and comparability is discussed in the following subsections. Typical calculations used in data quality measurements and data assessments are provided for reference in Attachment 1.

1.2 DEFINITION OF CRITERIA

This section defines how the project analytical measurement data objectives will be assessed for the project.

1.2.1 Precision

Precision measures the reproducibility of repetitive measurements and is usually expressed in terms of imprecision. It is strictly defined as the degree of mutual agreement among independent measurements as the result of the repeated application of the same process under similar conditions. Analytical precision is a measurement of the variability associated with duplicate (two) or replicate (more than two) analyses of the same sample extract in the laboratory and is determined by analysis of analytical duplicates. Total precision is a measurement of the variability associated with the entire sampling and analysis process. It is estimated by analysis of duplicate or replicate field samples and includes all possible sources of variability. Imprecision will be estimated using the relative percent difference (RPD) between the replicate samples. The frequency of collection for field duplicates is 10%.

Analytical precision goals are presented in documentation for each individual method. The field duplicate precision goal is $\leq$ 30% RPD. Uncontrollable matrix effects may confound the field duplicate evaluation and will be noted where identifiable. Results of these duplicate determinations will be used to evaluate the total imprecision possible in natural matrix sample results.

1.2.2 Accuracy

Accuracy is a statistical measurement of correctness, and includes components of random error (variability due to imprecision) and systematic error (bias). It, therefore, reflects the total error associated with a measurement. A measurement is accurate when the value reported does not differ from the true value. Analytical method accuracy is typically measured by determining the percent recovery of known target analytes that are spiked into a reagent water or soil (ongoing precision and recovery [OPR] sample) before extraction, at known concentrations. Additionally, $^{13}C_{12}$ labeled compounds are added to every sample and QC sample before extraction at known concentrations.

Both accuracy and precision are calculated for specific sampling or analytical batches, and the associated sample results must be interpreted considering these specific measures. An additional consideration in applying accuracy and precision is the concentration level of the

samples; a procedure capable of producing the same value within 50% would be considered precise for low level (near the detection limit) analyses of minor constituents, but would be unacceptable, and possibly useless, for major constituents at high concentrations.

Accuracy goals for OPRs and $^{13}C_{12}$ labeled compounds are presented in each method. Accuracy goals will be met if individual OPR and $^{13}C_{12}$ labeled compounds recoveries are within laboratory-derived acceptance criteria. OPR and $^{13}C_{12}$ labeled compound recoveries outside criteria indicate the analytical system is out of control and may require samples to be reanalyzed.

1.2.3 Completeness

Completeness is calculated from the aggregation of data for each method for any particular sampling event. For each method and each site, the number of valid results, divided by the number of individual analyte results initially planned for, expressed as a percentage, determines the completeness for the data set. The objective for completeness is 90 percent. If there are any instances of samples that could not be analyzed for any reason (holding time violations in which resampling and reanalysis were not possible, samples spilled or broken, etc.), the numerator of this calculation becomes the number of valid results minus the number of possible results not reported.

Valid results used to meet completeness objectives are those results that provide defensible estimates of the true concentration of an analyte in a sample. These valid results include data that is not qualified and data that QC results indicate qualification is necessary but which may still be used to meet project objectives. Invalid results are those data for which there is an indication that the prescribed sampling or analytical protocol was not followed.

The formula for calculation of completeness is presented below:

$$\% \text{ completeness} = \frac{\text{number of valid (i.e., non-R flagged) results}}{\text{number of possible results}}$$

1.2.4 Representativeness

Objectives for representativeness will be defined for each sampling and analysis task and will be a function of the investigative objectives. Representativeness will be achieved in part through use of the standard sampling and analytical procedures described in this QAPP, Work Plan, and the laboratory's Standard Operating Procedures (SOPs). The use of

equipment/rinseate blanks ensures that sample contamination is not present. Equipment/rinseate blanks will initially be collected at a frequency of 2% when unique sampling devices are not used for sample collection. The equipment/rinseate blanks will be retained until the analytical report is issued and the project team may elect to test on a case-by-case basis. The frequency of equipment/rinseate blank collection will be adjusted during the project, based on need.

1.2.5 Comparability

Comparability is the confidence with which one data set can be compared to other data sets. The objectives for this QA/QC program are to produce data with the greatest degree of comparability possible. Comparability will be achieved by using validated methods for sampling and analysis, reporting data in standard units, and using standard and comprehensive reporting formats.

1.3 GOALS

The overall project goal is to collect data sufficient for qualitative evaluation and future decisions. The QA objective (i.e., goal) is to have all analyses performed on an analytical system that is in statistical control and meets method specifications. Numerically, the goal is to have all individual results traceable to an OPR whose recovery is within laboratory-specified limits. Inaccurate or imprecise recovery of OPRs will potentially invalidate results.

This section describes the components of the sampling procedures that will be performed to meet the quality assurance objectives for the project.

2.1 SAMPLING PROTOCOLS

Detailed sampling protocols are provided and discussed in the Work Plan. Prior to beginning each sampling event, the field manager will ensure that the field personnel understand the purpose and objectives of the event. Topics of review and discussion with the team may include sampling locations, types of samples to be collected, number of samples collected, sample numbering, preservation requirements, parameter(s) to be analyzed, sampling procedures, equipment decontamination procedures, and chain-of-custody requirements.

2.2 SAMPLE HANDLING

The project manager is responsible for ensuring that samples are collected with properly decontaminated equipment and containerized in properly cleaned sample bottles. A summary of the recommended sample containers, volume, and preservation for each analytical method is provided in Table 2-1.

Soil and liquid extract samples will be retained until remedial decisions have been made, or the end of the calendar year in which the samples were collected, whichever is longer.

2.3 SAMPLING EQUIPMENT DECONTAMINATION

Equipment decontamination is an integral part of the data collection and QA process. The implementation of proper decontamination practices and procedures will begin in the field prior to use of sample collection equipment. All field sampling equipment will be decontaminated before use and after each sample location. Wash water and other fluids generated during decontamination will be managed at Dow's Wastewater Treatment Plant.

Table 2-1
Requirements for Containers, Preservation Techniques, and Sample Volumes

Name	Analytical Method [a]	Container [b]	Preservation	Minimum Sample Volume or Weight
% Moisture	EAC SOP	P,G	≤ 6°C	4oz. (s)
Dioxins and Furans	Method 8280 MAS/EPA 1613B[c]	P bag (s only), transferred in lab to G w/ Teflon-lined cap for long-term storage	≤ 6°C Freeze soil to ≤ -10°C for long-term storage	1 liter (w); 8 oz. (s)

[a] Comparable methods may be used with the approval of the project chemist.
[b] All containers are pretreated and cleaned before being purchased. Polyethylene (P); glass (G).
[c] EPA 1613B analyses will include a 2nd column confirmation for all Tetra-HexaCDD/F (only confirmation listed in the method documents are for 2378-TCDF).

C = Centigrade
s = Solid
w = Water

Sample possession during all sampling efforts must be traceable from the time of collection until the results are verified and reported. The sample custody procedures provide a mechanism for documentation of all information related to sample collection and handling to achieve this objective.

The field manager will be responsible for ensuring that the field team adheres to proper custody and documentation procedures for all sampling operations. Preformatted electronic chain-of-custody (eC-O-C) forms will be used as the primary documentation mechanism to track sample custody and analyses.

3.1 FIELD OPERATIONS

This section describes field procedures for maintaining sample custody. Other information describing field operations may be found in the Work Plan and its appendices. A summary of the recommended sample containers, volume, preservation, and hold times for each analytical method is provided in Table 2-1.

3.1.1 Field Records

Field personnel will be required to keep accurate written records of their daily activities in a bound logbook or with field forms. All entries will be legible, written in waterproof ink, and contain accurate and inclusive documentation of the team's activities, including instrument calibration, samples collected, field data and observations, any problems encountered, and actions taken to solve problems. Entry errors or changes will be crossed out with a single line and initialed by the person making the correction. Field logbooks or field forms will be available for review by the QA coordinator during systems audits or at any other time for QC checks by the field manager. This documentation provides verification of sampling procedures.

3.1.2 Sample Custody

The custody of the sample is maintained by:

- The sample is in the sampler's possession;
- The sample is in the sampler's view after being in possession;

- The sample was in the sampler's possession and then was locked up to prevent tampering; and
- The sample is in a designated secure area.

3.1.3 Sample Labels and Identification

Each sample container will receive a sample label. All samples shall be uniquely identified, labeled, and documented in the field at the time of collection. Sample labels will identify the sample by documenting the unique sample identification number, the sample type, the analytical method, the sampler's initials, date and time collected, the receiving laboratory, and the preservation method used. Sample labels will be computer-generated or hand written with a permanent marker and affixed to the sample container.

3.1.4 Chain-of-Custody Record

All sample ice chests will be accompanied by the C-O-C record, which identifies their contents. The original record plus one copy will accompany the ice chest; the other copy will be retained in the project file. One copy will be returned to the project team with the analytical results and the original is retained in the laboratory files with the analytical data.

The person relinquishing the samples to the facility will request the signature of a representative to acknowledge receipt of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Received By" space. When appropriate, as in the case of overnight shipment, the custody record should contain a statement that the samples were delivered to the designated location and the date and time noted.

All ice chests will be secured with custody seals for transportation to the off-site laboratory. Custody seals are not required for onsite analysis with the provision that the samples are delivered shortly after collection and that they will not be left unattended. Custody seals must be applied to all ice chests left unattended that contain samples.

The method of shipment, courier name(s), and other pertinent information is entered in the "Remarks" section when the samples are to be shipped (i.e., Federal Express, Express Mail, etc.) instead of hand delivered.

3.1.5 Shipping Procedures

The objective of sample handling procedures is to ensure that samples arrive at the laboratory intact, at the proper temperature, and free of external contamination. For all samples which will be shipped to the analytical service laboratory via overnight carriers, according to Department of Transportation standards, C-O-C procedures will be followed during transport.

Sample packaging requirements for hazardous materials requiring interstate transport is defined in the Code of Federal Regulations (CFR) 49, Chapter 1, and Part 171. These requirements outline in detail the proper classification and procedures for transportation of hazardous materials that will be used for transport of the samples. When samples are required to be stored at ≤ 6°C, generous amounts of ice will be packed with the samples. The ice will be of sufficient volume and will be distributed in the coolers so that the proper storage temperature will be maintained until the samples reach the laboratory. When the samples are delivered to the laboratory the temperature of each cooler of samples will be measured and recorded on the C-O-C form or addendum. The samples will be immediately placed in the sample control refrigerator after sample log in.

The following procedures will be used to prevent bottle breakage and cross contamination:

- All samples will be transported inside hard plastic coolers;
- All glass bottles will be protected to prevent glass to glass contact;
- The coolers will be taped shut and sealed with custody seals to indicate unauthorized opening of the cooler; and
- Samples that are known or suspected to contain high levels of chemical constituents (based on past monitoring data or observation) will be packaged and transported separately from other samples.

3.2 LABORATORY OPERATIONS

The analytical service laboratory will follow SOPs for handling, identification, control, and C-O-C procedures and to maintain the validity of the samples. These SOPs are based on the use of a laboratory information management system (LIMS), which is for tracking samples from receipt through reporting of the analytical results.

3.2.1 Sample Handling

The following section describes the activities related to sample receipt, storage, and tracking.

- Upon receipt, the sample custodian will inspect all sample containers for integrity. The presence of leaking or broken containers or custody seals will be noted on the C-O-C form. The sample custodian will sign the C-O-C form (with date and time of receipt), thus assuming custody of the samples.
- The information on the C-O-C form will be compared with that on the sample tags and labels to verify sample identity. Any inconsistencies will be resolved with the project chemist (or field team member) before sample analysis proceeds.
- The temperature of incoming coolers of samples will be checked and the temperature recorded on the internal C-O-C record.
- Preserved samples (i.e., those requiring pH adjustments) will be checked and any improperly preserved samples noted on the C-O-C.
- Samples will be moved to a controlled sample storage refrigerator for storage prior to analysis.
- Document control will retain a legible copy of the original C-O-C form.

Samples will be maintained in storage refrigerators at ≤ 6°C prior to sample preparation and analysis. Analytical laboratory personnel will request or check out samples for analysis from the sample custodian (if a different person).

If samples are known or suspected to be highly contaminated, laboratory sample control will be notified, so those samples can be stored separately from less contaminated samples, minimizing the potential for cross contamination.

3.2.2 Sample Identification

As samples are logged into the laboratory sample tracking system each sample is assigned a unique sample control number and is correlated with the field sample numbers obtained from the field C-O-C forms, as both numbers are entered into the system for a given job. Analytical requirements for each sample are entered into the computer. A hard copy of the work order and other information is printed and filed with the received documentation. Labels are printed with sample information and secured to each sample. Data sheets and

work sheets are printed for each batch of samples and are distributed to the appropriate laboratory managers.

3.2.3 Sample Custody Records

Sample custody and documentation in analytical laboratories are organized around sample and analysis management systems. For example, these systems are computer software systems specifically designed for tracking and handling the large amount of information required for the efficient management of an analytical chemistry laboratory.

Following sample log in, the samples are placed in a designated secured storage area. Samples are maintained at ≤ 6º C from the time of receipt until the analyses are complete. Samples in freezers are maintained at less than 0°C from the time of receipt until the analyses are complete. Subsequent sample custody and all transactions are documented. Sample custody is documented according to the laboratory SOP.

The analyst receives the samples from sample control and completes the sample work sheets or custody sheet. After analysis, the sample is returned to the designated storage location in sample control. The sample is stored until the assigned time or written permission is given to either properly dispose of or return the sample to the client. All sample documentation is maintained in secure storage in a controlled access area.

This section contains brief descriptions of calibration procedures and analytical methodologies used for the analysis of soil samples that will be collected for this investigation.

4.1 IDENTIFICATION OF METHODS

Methods to be used for sample analysis are presented in Table 4-1. Method 8280 MAS will be the primary method used for the analysis of the target dioxins and furans. It is based upon modifications to EPA Method SW8280B. EPA Method 1613B with 2nd column confirmation for all Tetra-HexaCDD/Fs will be used to make remedial decisions for samples in the range of >220 and ≤280 (as determined by Method 8280 MAS); and will also serve as the confirmation method for the analysis of dioxins and furans. The laboratory will follow the QC procedures as specified in Methods 8280 MAS and EPA Method 1613B. All soil sample results must be reported as dry weight.

4.1.1 Analytical Batch Size

The analytical batch size for the project will be limited to no more than forty (40) samples. Modification of the analytical batch size may be completed during the project based on performance metrics described in Sections 4.3.2 (calibration verification), 4.4.1 (OPR), 4.4.3 ($^{13}C_{12}$ labeled compounds), 4.4.4 (method blank) and Table 5-2 of this Plan. Justification for changes to the batch size will be maintained in the project QA file.

4.2 DETECTION AND QUANTITATION LIMITS

This section presents and defines limits to be used in describing detectable concentrations. All soil sample results must be reported as dry weight. All sample-specific estimated detection limits (EDLs) and method quantitation limits (MQLs) must be corrected for dry weight (if applicable), dilution factors, sample size, and any other factors applied to the field sample result.

4.2.1 Estimated Detection Limits

The EDL will be calculated on a per analyte and sample basis. The EDL will be extrapolated from the detection verification standard (DVS; see Method 8280 MAS).

4.2.2 Method Quantitation Limits

The MQL is defined by the DVS. All results shall be reported at or above the EDL values. For results falling between the EDL and the MQL, a "J" flag (as estimated) shall be applied by the laboratory to the results indicating the variability associated with the result. No results shall be reported below the EDLs. Target MQLs are presented in Table 4-2.

Table 4-2
Target Method Reporting Limits

Analyte	CAS Number	Soil (ng/kg)
EAC-SOP, % Moisture	NS	NS
Method 8280 MAS, Dioxins and Furans[a]		
1,2,3,4,6,7,8-HpCDD	35822-46-9	25
1,2,3,4,6,7,8-HpCDF	67562-39-4	25
1,2,3,4,7,8-HxCDD/1,2,3,6,7,8-HxCDD	39227-28-6/57653-85-7	20
1,2,3,4,7,8-HxCDF/1,2,3,6,7,8-HxCDF	70648-26-9/57117-44-6	20
1,2,3,7,8,9-HxCDD	19408-74-3	10
1,2,3,7,8-PeCDD	40321-76-4	10
2,3,4,7,8-PeCDF	57117-31-4	10
2,3,7,8-TCDD	1746-01-6	10
2,3,7,8-TCDF	51207-31-9	10
OCDD	3268-87-9	50
OCDF	39001-02-0	50
EPA 1613B, Dioxins and Furans[b]		
2,3,7,8-TCDD	1746-01-6	1
1,2,3,7,8-PeCDD	40321-76-4	5
1,2,3,6,7,8-HxCDD	57653-85-7	5
1,2,3,4,7,8-HxCDD	39227-28-6	5
1,2,3,7,8,9-HxCDD	19408-74-3	5
1,2,3,4,6,7,8-HpCDD	35822-39-4	5
OCDD	3268-87-9	10
2,3,7,8-TCDF	51207-31-9	1
1,2,3,7,8-PeCDF	57117-41-6	5
2,3,4,7,8-PeCDF	57117-31-4	5
1,2,3,6,7,8-HxCDF	57117-44-9	5
1,2,3,7,8,9-HxCDF	72918-21-9	5
1,2,3,4,7,8-HxCDF	70648-26-9	5
2,3,4,6,7,8-HxCDF	60851-34-5	5
1,2,3,4,6,7,8-HpCDF	67562-39-4	5
1,2,3,4,7,8,9-HpCDF	55673-89-7	5
OCDF	39001-02-0	10

[a] Reporting Limits for Method 8280 MAS
[b] Target Quantitation Limits for Method 1613b

CAS = Chemical Abstract Service
EPA = United States Environmental Protection Agency
ng/kg = Nanogram per kilogram
NS = Not specified
SOP = Standard Operating Procedure

4.3 INSTRUMENT CALIBRATION REQUIREMENTS

The compliance requirements for satisfactory instrument calibration ensure that the instrument is capable of producing acceptable quantitative data. Records of standard preparation and instrument calibration shall be maintained. Records shall unambiguously trace the preparation of standards and their use in calibration and quantitation of sample results. Calibration standards shall be traceable to standard materials. Instrument calibration for the method shall be checked using all of the target analytes. They consist of an initial calibration to demonstrate that the instrument is performing acceptably throughout the analytical working range before project samples are analyzed, and continuing calibration verification checks that document that the initial calibration is still valid, and that satisfactory maintenance and day-to-day adjustment of the instrument have been achieved. Specific control criteria and corrective action requirements for initial and continuing calibration verification checks are presented Methods 8280 MAS and EPA 1613B.

4.3.1 Initial Calibration

The initial calibration will be performed for all target analytes. Changes in the instrumental set-up or responses outside of acceptance criteria will require a recalibration. A QC check sample containing all target analytes (from a different supplier than the standards used in the calibration curve) and at a concentration in the midpoint of the calibration curve must be analyzed to verify initial calibration. Instrumentation will be recalibrated with each new lot of $^{13}C_{12}$ labeled standards.

Additional calibration QC parameters and their respective acceptance criteria are listed in Tables 5-2 and 5-3.

4.3.2 Calibration Verification

With each batch of samples a Calibration Verification Standard (CVS) will be analyzed by using a mid-range calibration standard. A quantification of the samples in the associated set will only be performed if this CVS is within the acceptance criteria.

Additional calibration QC parameters and their respective acceptance criteria are listed in Tables 5-2 and 5-3.

4.4 ELEMENTS OF QUALITY CONTROL

This section presents QC requirements relevant to analysis of environmental samples that shall be followed during all analytical activities producing definitive data. The purpose of this QC program is to produce data of known quality that satisfy the project objectives and that meet or exceed the requirements of the standard methods of analysis. This program provides a mechanism for ongoing control and evaluation of data quality measurements through the use of QC materials.

Laboratory QC samples (e.g., blanks and OPRs) shall be included in the preparation batch with the field samples. A preparation batch is a number of samples (not to exceed 40 environmental samples plus the associated laboratory QC samples) that are similar in composition (matrix) and that are extracted at the same time and with the same lot of reagents. The identity of each preparation and analytical batch shall be unambiguously reported with the analyses so that a reviewer can identify the QC samples and the associated environmental samples.

The type of QC samples and the frequency of use of these samples are discussed below and in the specific methods.

4.4.1 Ongoing Precision and Recovery (OPR) Sample

The OPR sample is an analyte-free sand or soil spiked with all project-specified analytes for the method. Each analyte in the OPR sample shall be spiked at a level approximately equal to the midpoint of the calibration curve for each analyte. The OPR sample shall be carried through the complete sample preparation and analysis procedure. The OPR is used to evaluate each batch and to determine if the method is in control. The OPR sample cannot be used as the CVS.

One OPR sample shall be included in every preparation batch. If more than one OPR sample is analyzed in a batch, results from all OPR samples analyzed shall be reported. Laboratory-derived acceptance criteria will be used and checked annually. Data will be rejected if these values are not met. A QC failure of an analyte in any of the OPR samples shall require appropriate corrective action, including qualification of the failed analyte in all of the associated samples.

If an OPR fails, an attempt must be made to determine the source of error and find a solution. All of the analytes that were subject to corrective action in the OPR and all of the samples in

the batch be reprepared and reanalyzed. The corrective action applied shall be based on professional judgment in the review of other QC measures (i.e., internal standards). If an analyte falls outside the OPR acceptance criteria a second time or if there is not sufficient sample material available to be reanalyzed, then all the results in the associated batch for that analyte must be flagged. The recoveries of those analytes subject to corrective action must be documented in the case narrative, whether flagging is needed or not. When an analyte in an OPR exceeds the acceptance criteria and no corrective action is performed or the corrective action was ineffective, the appropriate validation flag, as described in Section 6.0, shall be applied to all affected results.

4.4.2 Field Replicates (FRs)

A field replicate (FR) sample is a second or multiple sample(s) collected at the same location as the original sample. Replicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis. All DUs will have two (2) replicates collected (three total samples), but not all will be tested. If the first sample result by MAS 8280 is greater than 220 ppt TEQ and less than or equal to 280 ppt TEQ, both the first sample and the replicates will be tested according to EPA Method 1613b with second column confirmation.

If no MAS 8280 results are within the range specified above, replicate sample results are used to assess precision of the sample collection process. The frequency of collection for field replicates is 10%, biased to samples closest to 250 ppt. Two areas are planned for investigation (North Area and East Area). Replicates should be equally representative of those two areas. Field replicate results that are greater than the MQLs in at least one sample of the field replicate pair are used to assess precision. The RPD acceptance criterion for soil samples is $\leq$30%. If this acceptance criterion is not met, then the analyte in the parent sample and the field duplicate sample are qualified according to the data flagging criteria in Section 6.0.

4.4.3 $^{13}C_{12}$ Labeled Compounds

A mixture of stable isotopically labeled analogs of 17 of the dioxins/furans is added into each sample and QC sample before extraction. They are used to assess method performance on the sample matrix.

When the $^{13}C_{12}$ labeled compound results are outside of the acceptance limits, corrective actions shall be performed. Check for system problems and correct. If there are obvious

matrix problems, flag data. If there are no obvious matrix problems, reanalyze affected samples. If corrective actions are not performed or are ineffective, the appropriate validation flag, as described in Section 6.0, shall be applied to the sample results.

4.4.4 Method Blank (MB)

A method blank (MB) is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. It shall be carried through the complete sample preparation and analytical procedure and is used to document contamination resulting from the analytical process. A MB shall be included in every preparation batch.

The presence of analytes in a MB at concentrations equal to or greater than the MQL indicates a need for corrective action. Corrective action shall be performed to eliminate the source of contamination. No analytical data shall be corrected for the presence of analytes in blanks. When an analyte is detected in the MB and in the associated samples and corrective actions are not performed or are ineffective, the appropriate validation flag, as described in Section 6.0, shall be applied to the sample results.

4.4.5 Equipment Blank (EB)/Rinsate Blank (RB)

An equipment blank (EB) or rinsate blank (RB) is a sample of ASTM Type II reagent grade water poured into or over or pumped through the sampling device, collected in a sample container, and transported to the laboratory for analysis. EBs are used to assess the effectiveness of equipment decontamination procedures.

Equipment/rinseate blanks will initially be collected at a frequency of 2% when unique sampling devices are not used for sample collection. The equipment/rinseate blanks will be retained until the analytical report is issued and the project team may elect to test on a case-by-case basis. When an analyte is quantified in the EB the appropriate validation flag, as described in Section 6.0, shall be applied to all sample results from samples associated with the sampling device. The frequency of equipment/rinseate blank collection will be adjusted during the project, based on need.

4.4.6 Additional QC Parameters

Other additional QC parameters are specified in Method 8280 MAS and EPA 1613B. Clarification of specific practices (where different from those listed or suggested in the

methods) are noted in this Plan. Appropriate data validation flags will be assigned to results that do not meet the acceptance criteria specified in this Plan.

4.4.7 Split Sampling Procedures

Michigan Department of Environmental Quality (DEQ) staff will periodically split some samples as part of their oversight of this project. Data generated from DEQ split samples will be used to monitor the overall quality of project analytical work. The laboratories used during this project will use different analytical methods, and some differences are anticipated. A comparability study between Dow analyzed samples and agency analyzed samples is being conducted prior to the start of this project.

Laboratory QC is necessary to control the analytical process, to assess the accuracy and precision of analytical results, and to identify assignable causes for atypical analytical results. QC is achieved by collecting and/or analyzing a series of duplicate, replicate, blank, spike, and spike duplicate samples to ensure that the analytical results are within QC limits specified by the program. Laboratory QC samples are documented at the bench and reported with the analytical results. The QC sample results are used to quantify precision and accuracy and identify any problems or limitations associated sample results.

5.1 CONTROL LIMITS

QC control limits and procedures are presented by method in the following tables. The laboratory may use laboratory-derived acceptance criteria. Laboratory-derived acceptance criteria must be checked annually. The required corrective action guidelines to be followed are also presented in the following tables when results fall outside the prescribed QC limits. The corrective action activities listed are to be used as guidelines and are not necessarily followed in the order listed. The primary intent of these guidelines is to identify any problems and correct the problem before proceeding.

Table 5-1
Summary of Calibration and Internal QC for Moisture

Quality Control Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Calibration – Every six months	Test with ASTM ULTRA Class weights at 1500 g and 3000 g.	+0.05 g	1. Recalibrate. 2. If still out, repair balance and recalibrate.
Calibration Verification – Daily	Using Global-SOP-00602.05 Scales are tested with ASTM ULTRA Class weights at 200 g and 2000 g.	200g – +0.004 2000g – +4.00	1. Repeat calibration 2. If still out, identify and correct problem, then recalibrate. 3. If still out, repair balance.
Oven Temperature Check – Every sample set	Test oven temperature when before samples are put into oven and before sample are removed from oven. Record date, time, and temperature.	100°C – 110°C	Adjust temperature to within limits

Table 5-2
Summary of Calibration and Internal QC for Method 8280 MAS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Precision and Recovery	Significant change in instrumentation	Laboratory-derived acceptance criteria.	Correct problem, re-extract and reanalyze.
Initial calibration (ICAL)	Minimum 5-point calibration curve using isotope dilution	Use average response factor if <20% relative standard deviation (RSD). If >20% RSD, then use linear regression curve.	No analyses until acceptance criteria are met.
Quality Check Standard (QC)	After each ICAL	Laboratory-derived acceptance criteria.	Correct problem and reanalyze ICAL.
Calibration verification standard (VER)	Every 12 hours	Ion ratios must be within limits listed in Table 6. Verification must be within limits listed in Table 4 of Method 8280 MAS.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Ion abundance	Each sample	Ion ratios must be within limits listed in Table 6 of Method 8280 MAS.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Isomer specificity	Daily using calibration verification standard (VER)	Adequate separation between ^{13}C 2,3,7,8-TCDF and native 2,3,7,8-TCDD.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Analyte identification	For each component and sample	As per Method 8280 MAS Section 10.9 (qualitative) or Section 10.10 (quantitative).	N/A
Isotopic ratio measurements for dioxins/furans	For each component and sample	As per Method 8280, Section 9.4.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Retention time windows	N/A for isotope dilution	N/A for isotope dilution.	N/A
Detection verification standard (DVS)	Every 12 hours	As per 8280 MAS, Section 10.8.2.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Method blank (MB)	One MB per preparation batch	Must not exceed MQL.	Correct problem and rerun.
Ongoing Precision and recovery (OPR) standard for all compounds.	One OPR per preparation batch	Laboratory-derived acceptance criteria.	Correct problem, re-extract, and reanalyze .
Labeled Compound Recovery Standards	Each sample and QC sample	Recoveries: 5%-100%.	Correct problem, re-extract, and reanalyze .

Table 5-3
Summary of Calibration and Internal QC for Method EPA 1613B

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Precision and Recovery	Once per analyst or significant change in instrumentation	Laboratory-derived acceptance criteria.	Correct problem, re-extract and reanalyze.
Initial calibration (ICAL)	Minimum 5-point calibration curve using isotope dilution	Use average response factor if <20% relative standard deviation (RSD). If >20% RSD, then use linear regression curve.	No analyses until acceptance criteria are met.
Quality Check Standard (QC)	After each ICAL.	Laboratory-derived acceptance criteria.	Correct problem and reanalyze ICAL.
Calibration verification standard (VER)	Every 12 hours.	As per Method 1613b, Section 15.3.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Ion abundance	Daily using detection verification standard (DVS)	As per Method 1613b, Section 10.2.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Isomer specificity	Daily using calibration verification standard (VER)	As per Method 1613b, Section 10.4.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Analyte identification	For each component and sample	As per Method 1613b, Section 16 (qualitative) or Section 17 (quantitative).	N/A
Isotopic ratio measurements for dioxins/furans	For each component and sample	As per Method 1613b, Section 17.	Adjust instrument and reanalyze. No analyses until acceptance criteria are met.
Method blank (MB)	One MB per preparation batch	Must not exceed MQL.	Correct problem and rerun.
Ongoing Precision and recovery (OPR) standard for all compounds.	One OPR per preparation batch	Laboratory-derived acceptance criteria.	Correct problem, re-extract, and reanalyze.
Labeled Compound Recovery Standards	Each sample and QC sample	As per Method 1613b, Table 7.	Correct problem, re-extract, and reanalyze.
Cleanup standard	Optional, for each sample and QC sample	As per Method 1613b, Table 7.	Correct problem, re-extract, and reanalyze.

The data reduction, validation, and reporting procedures described in this section will ensure that complete documentation is maintained, that transcription and data reduction errors are minimized, the quality of the data is reviewed and documented, and the reported results are properly qualified.

6.1 DATA MANAGEMENT

The primary data management activities will include:

- Data transfer from field and laboratory activities to a project filing system;
- Data management to ensure that data are stored and output in a manner that continues the C-O-C;
- Requirements of review to ensure that plans for data collection were fulfilled;
- Analytical data validation which will report data to be used for interpretation activities; and
- Reporting functions may include outputting data for report tables, statistical analysis, interpretation, and electronic transfer.

A computerized project database will be used for data management on the project. The proposed database will be implemented in relational data management software. The database is used to store, transfer, and report analytical data. A series of programs allows electronic reporting of data. The laboratory is responsible for generating hard copies and electronic files for the analytical results. Both the hardcopy analytical reports and electronic data files are transferred to the project QA coordinator and/or data management staff. The laboratory provides additional documentation regarding C-O-C procedures, etc. that are not transmitted via electronic files.

6.2 DATA REDUCTION

The laboratory analyst is responsible for the reduction of raw data generated at the laboratory bench. The data interpretation that is required to calculate sample concentrations follows the methodology described in the specific analytical SOP. After all analyses have been completed and reported, the laboratory manager or designee reviews the raw data and verifies that the analyses were properly performed and reported. All non-detected results must be reported as < EDL. A value that is reported between the EDL and the MQL must be flagged ("J") by the laboratory to indicate that the number is an estimate. Blank results below the

MQLs cannot be controlled by the laboratory. The laboratory manager may then transfer the raw data to the document control area, where the raw data are filed if needed for a subsequent QC review. Raw data, together with all supporting documentation, are stored in confidential files by document control.

After all analyses for a report are complete, the data are entered into the laboratory reporting system and a preliminary report is generated for review by the laboratory managers. This review is followed by a quality check carried out by the document control group to verify that the QC meets the specifications of the method. Data qualifiers shall be added or, if applied by a software package, reviewed by the laboratory manager. A case narrative shall be included with each data report package to explain any nonconformance or other issues.

Identification of outliers is also a part of the data review. An outlier is an unusually large (or small) value in a set of observations. There are many possible reasons for outliers including:

- Faulty instruments or component parts;
- Inaccurate reading of a record, dialing error, etc;
- Errors in transcribing data; and
- Calculation errors.

Sometimes analysts or operators can identify outliers by noting the above types of occurrences when they record the observations. In these instances, the errors are corrected, or if correction is not possible, the suspect observations may be removed from the data before calculations are performed. If no such information exists, the statistical evaluation techniques are used to test suspected outliers at the five percent significance level if there are three or more points in the data set containing the outlier. Outliers identified by this method may be removed from the data before further processing.

Laboratory concentration data will be reported using three significant figures for statistical calculations. Remedial decisions and external reports will be made using two significant figures.

6.3 DATA QUALITY ASSESSMENT

Validation of the laboratory reports and sample custody documentation will be performed to ensure all samples were analyzed as requested. The laboratory reports are reviewed for the following:

- Sample hold times;
- Target analyte list;
- Reporting limits;
- Reporting units;
- Laboratory blanks;
- Field duplicates;
- OPR results; and
- Other applicable QC results.

The data validation task that will be performed in support of the project work will consist of reviewing three areas of data quality. The QC checks used to assess measurement precision are field duplicate samples. The QC checks used for the assessment of measurement accuracy are OPRs and surrogate spikes. The results for field and laboratory (i.e., method) blanks are the third group of QC data reviewed.

6.4 DATA VALIDATION AND REPORTING

The Project QA Coordinator, or other QA staff, will review and summarize all QC sample results to evaluate the sampling and analytical performance. Blank results will be evaluated to identify any systematic contamination; spike and duplicate results will be compared to the QA objectives presented in Section 1, and the results used to calculate precision and accuracy for the data set. This process will identify analytical methods and analytes for which the QA objectives are not satisfied and corresponding sample data will be qualified with a "flag" indicating the problem. Samples collected on the same day, or analyzed in the same run or batch, or individual samples may be flagged, depending on the type of problem that has been identified. Reanalysis or resampling may be recommended as a corrective action at this time if data are determined to be unacceptable for the intended application.

A data validation report will be submitted by the data validator summarizing the result of the data quality assessment. The measurement data will be discussed and qualified as appropriate based on the QC results. For example, a laboratory blank contamination will influence all samples extracted or analyzed on a specific day or during a specific analytical run. Data validation flags will be assigned to the data. Data validation flags, codes, and descriptions are presented in Table 6-1.

Table 6-1
Data Qualifier Definitions

Qualifier	Definition	When Assigned:
B	Reported result is similar to associated blank concentration and is not considered representative of actual site conditions.	This qualifier is assigned when a sample result is equal to or less than five times the associated blank result.
J	Reported result is an estimate.	This qualifier is assigned when unacceptable precision is demonstrated, if there are chromatographic interferences, if conflicting data exists about whether or not the sample result is biased high or low, or if an internal standard does not meet acceptance criteria. It also can indicate that the value is between the laboratory's EDL and MQL. A code indicating a low or high bias may be used in conjunction with this flag.
H	Reported result is potentially biased high.	This qualifier is assigned when unacceptable accuracy is demonstrated for high OPR recoveries, high internal standards, high surrogate recoveries, or high calibration verification checks.
L	Reported result is potentially biased low.	This qualifier is assigned when unacceptable accuracy is demonstrated for low OPR recoveries, low surrogate recoveries, missed hold times, or low calibration checks.
UJ	The analyte was not detected above the EDL, but may still be present.	This qualifier is assigned when unacceptable precision is demonstrated, when a sample receipt condition is compromised, a sample is analyzed past hold time, or if an internal standard does not meet acceptance criteria. A code indicating a low bias may be used in conjunction with this flag.
R	Reported result is unusable for its intended purpose.	This qualifier is assigned when an OPR or surrogate compound is recovered below 5% and the sample results were not detected. It also is used when hold times are grossly missed.

EDL = Estimated detection limit
MQL = Method quantitation limit
OPR = Ongoing performance and recovery

A QA audit is an independent appraisal of a measurement system. It typically includes a performance evaluation using apparatus and/or standards that are different from those used in the measurement system. It also may include an evaluation of the potential of the system to produce data of adequate quality to satisfy the objectives of the measurement efforts. The independent, objective nature of the audit requires that the auditor be functionally independent of the sampling/analytical team.

Quality assurance audits play an important role in an overall QA/QC program. This section describes the role of the QA auditor and the nature of both systems and performance audits.

While this is not required at this time by the client, these audits can be requested by the client in order to ensure that the data quality is acceptable.

Attachment 1
Statistical Calculations

Statistic	Symbol	Formula	Definition	Uses
Mean	$\overline{X}$	$\frac{\left(\sum_{i=1}^{n} x_i\right)}{n}$	Measure of central tendency	Used to determine average value of measurements
Standard Deviation	S	$\left(\frac{\Sigma(x_i-\overline{x})^2}{(n-1)}\right)^{½}$	Measure of relative scatter of the data	Used in calculating variation of measurements
Relative Standard Deviation	RSD	$(S/\overline{X}) \times 100$	Relative standard deviation, adjusts for magnitude of observations	Used to assess precision for replicate results
Percent Difference	%D	$\frac{x_1 - x_2}{x_1} \times 100$	Measure of the difference of 2 observations	Used to assess accuracy
Relative Percent Difference	RPD	$\left(\frac{(X_1 - X_2)}{(X_1 + X_2)/2}\right) \times 100$	Measure of variability that adjusts for the magnitude of observations	Used to assess total and analytical precision of duplicate measurements
Percent Recovery	%R	$\left(\frac{X_{meas}}{X_{true}}\right) \times 100$	Recovery of spiked compound in pure matrix	Used to assess accuracy
Percent Recovery	%R	$\frac{\left(\begin{array}{c}\text{value of}\\ \text{spiked}\\ \text{sample}\end{array} - \begin{array}{c}\text{value of}\\ \text{unspiked}\\ \text{sample}\end{array}\right)}{\text{Value of added spike}} \times 100$	Recovery of spiked compound in sample matrix	Used to assess matrix effects and total precision
Correlation Coefficient	R	see SW8000B Section 7.5.3		Evaluation of "goodness of fit" of a regression line
Coefficient of Determination	COD	see SW8000B Section 7.5.3		Evaluation of "goodness of fit" of a polynomial equation

n = Number of observations
x = Observation (concentration)