REVISED QUALITY ASSURANCE PROJECT PLAN FOR THE ECOLOGICAL RISK ASSESSMENT OF DIOXINS PRESENT IN THE TITTABAWASSEE RIVER AND FLOODPLAIN

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Definitions and Acronyms

95% UCL	95-percent upper confidence limit
ASTM	American Society for Testing and Materials
COC	Chain-of-custody
CUR	Condition upon receipt report
DQO	Data quality objective
Dup	Duplicate
EDD	Electronic data deliverable
ERB	Equipment rinsate blank
FTL	Field team leader
GC	Gas chromatograph
GIS	Geographic Information Systems
HASP	Health and safety plan
HRGC/HRMS	High Resolution Gas Chromatography/High Resolution Mass Spectrometry
IDL	Instrument detection limit
LCS	Laboratory control samples
LOQ	Limit of Quantitation
MCL	Maximum contaminant levels
MDEQ	Michigan Department of Environmental Quality
MDL	Method detection limit
µg	Microgram
mg	Milligram
mL	Milliliter
MS	Mass spectrometer
MS/MSD	Matrix spike/matrix spike duplicate
MSU	Michigan State University
NIST	National Institute of Standards and Technology
PARCCS	Precision accuracy representativeness comparability completeness sensitivity
PCBs	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans
QA	Quality assurance
QAMP	Quality assurance management plan
QAPP	Quality Assurance Project Plan
QC	Quality control
RL	Reporting limit
RPD	Relative percent difference
RRT	Record retention time
SDG	Sample delivery group
SOP	Standard operating procedure
SRM	Standard reference material
SSO	Site safety officer
TAL	Target analyte list
USEPA	United States Environmental Protection Agency

1.0 INTRODUCTION

The purpose of this document is to present the quality assurance/quality control (QA/QC) requirements for the investigations described herein. This Quality Assurance Project Plan (QAPP) has been prepared in accordance with the guidance manuals "EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations" (EPA QA/R-5) (USEPA, 1994a), "Guidance for Quality Assurance Project Plans" (EPA QA/G-5) (USEPA 1998), and "Guidance for the Data Quality Objectives Process" (EPA QA/G-4) (USEPA, 1994b).

To provide a consistent framework, the format of this document closely follows the specifications and instructions for information as presented in EPA QA/R-5, which identifies four elements that must be addressed in a QAPP. The four elements (termed "groups") and their locations in this document are:

- **Group A, Project Management.** A discussion of this element can be found in Section 2.0 of the QAPP. The objective of this section is to provide an overview of project management, including project history and objectives, roles and responsibilities.
- **Group B, Measurement/Data Acquisition.** This element is presented in Section 3.0 of the QAPP. This section covers all aspects of measurement systems design and implementation.
- **Group C, Assessment/Oversight.** This element addresses the activities associated with assessing the effectiveness of the implementation of the project and associated QA/QC. It is discussed in Section 4.0 of the QAPP.
- **Group D, Data Validation and Usability.** Section 5.0 of the QAPP covers the QA activities that occur after the data collection phase of the project is completed.

2.0 PROJECT MANAGEMENT

This section provides the overall approach to managing the investigations and addresses the following:

- Project organization and roles and responsibilities.
- Problem definition.
- Problem description.
- Project Data Quality Objectives (DQOs) and criteria for measurement data.
- Special training requirements or certificates required for work performed.
- Documentation and records management.

2.1 Project Organization and Roles and Responsibilities

This section contains descriptions of the project roles and responsibilities for the principal project team members. The combined strengths of MSU and ENTRIX, Inc. is presented in Figure 2-1. Figure 2-2 and Figure 2-3 presents the project organization charts for ENTRIX and MSU, respectively.

The project team assembled for these studies combines the skills and expertise of both the Aquatic Toxicology Laboratory (ATL) at Michigan State University (MSU) and ENTRIX Inc (Figure 2-1). ATL personnel have a wealth of experience in conducting the field studies and chemical analyses required to carry out the project. ENTRIX Inc. brings a wealth of skills and experience in project management, document control, data analysis and risk assessment.

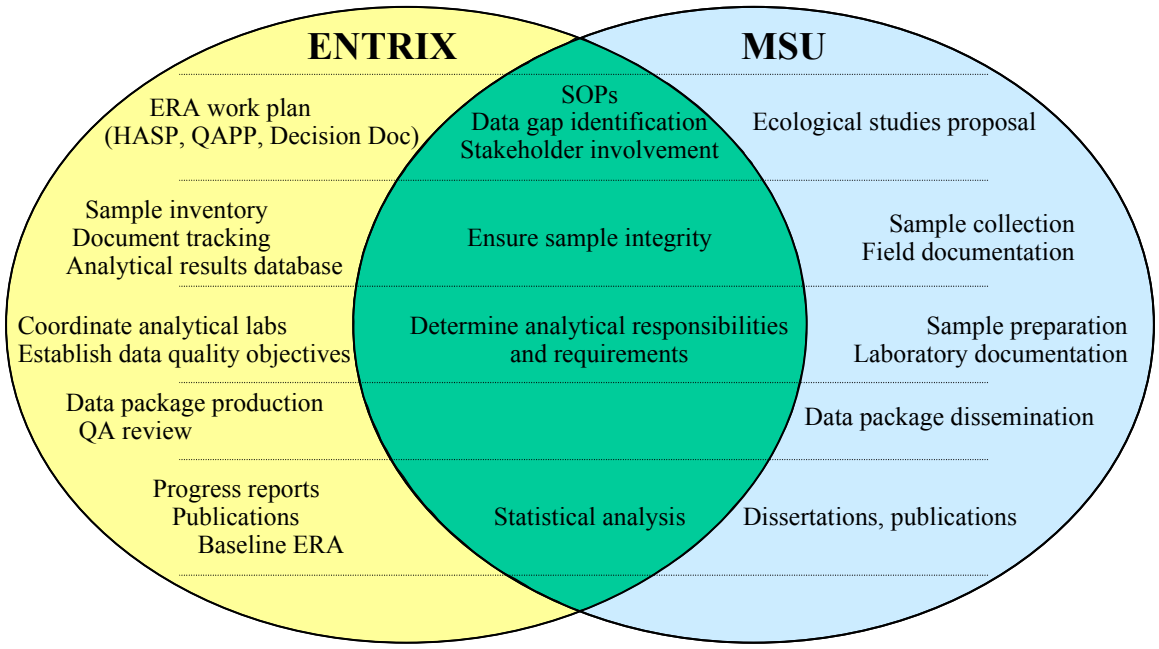

Figure 2-1. Combined Strengths of Michigan State University and ENTRIX Personnel

Project Manager — Prof. John P. Giesy (MSU) will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments related to Michigan State Univer**r**sity activities to accomplish program QA objectives; and act as liaison between agencies, field staff, and the sponsor Project Manager.

Quality Assurance (QA) Auditor — (To Be Named) An independent advisor will review all QA activities to ensure compliance with contract specifications. The auditor will review all data deliverables to ensure data quality and usability. The identity of this person or persons will be determined by discussion with the sponsor and all involved stakeholders.

Field Team Leader (FTL) — Dr. Matthew Zwiernik (MSU) will oversee field activities and supervise the field crews. The FTL will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The FTL will discuss field activities with the Project Manager.

Laboratory Project Manager — Mr. Patrick Bradley (MSU) is responsible for assuring that the analysis of all samples collected is performed in accordance with the QAPP and the laboratory's quality assurance manual. The Laboratory Project Manager is the liaison between the laboratory staff and is responsible for keeping the project director and the laboratory informed of project status. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

Quality Assurance (QA) Manager – Prof. Paul Jones (MSU) will initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors. The manager will review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, the QA manager will approve corrective actions. The QA manager will report quality non-conformances to the Project Manager and review all pertinent portions of the both MSU and ENTRIX deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Project Coordinator/Data Manager – Dr. Denise Kay (ENTRIX) will coordinate ENTRIX activities on the project. These will include data and documentation preparation and dissemination. She will be responsible for the structure, organization, format, implementation, and operation of the study plan databases. A central project database will be constructed using object linking and embedding by accessing the individual study plan databases. She will also be responsible for preparation of data deliverables.

ENTRIX Inc. Project Director – Dr. Alan Blankenship (ENTRIX) will be responsible for compilation of summary results and project final reports. He will also be responsible for statistical analysis and risk assessment.

Data Interpretation - Dr John Newsted (ENTRIX) will be responsible for statistical analysis, reporting of data and risk assessment.

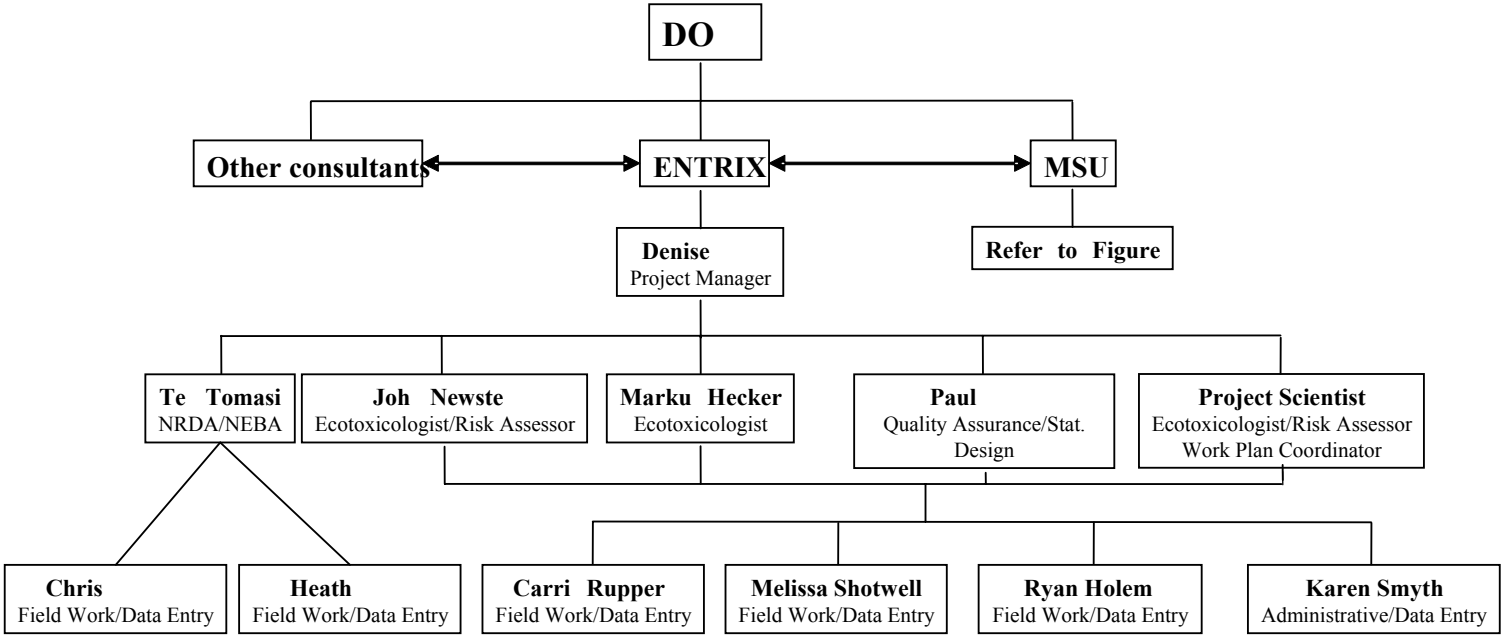

Figure 2-2. Project Organizational Chart - ENTRIX

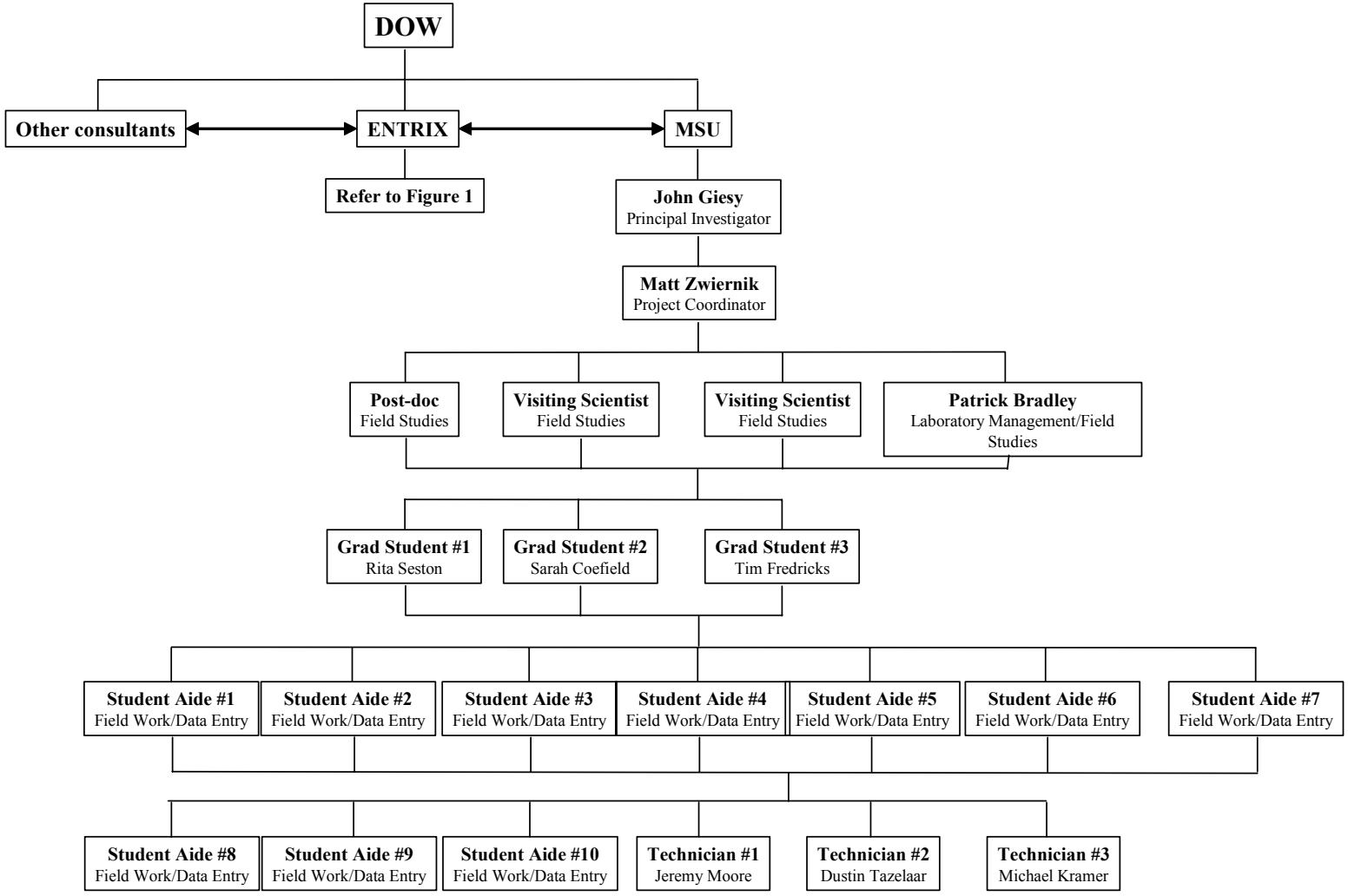

Figure 2-3. Project Organizational Chart - MSU

2.2 Problem Definition

The Ecological Risk Assessment (ERA) is designed to quantify the degree of risk posed to organisms exposed to PCDD/Fs in the Tittabawassee River floodplain. The study will determine the nature and extent of exposure and the potential for adverse ecological effects in wildlife.

The Tittabawassee River study area, hereafter referred to as the "Site", includes sediments and floodplain soils for approximately 23 miles of the Tittabawassee River downstream of Midland, Michigan. Specifically, the Site includes the upstream boundary of The Dow Chemical Company to the confluence of the Tittabawassee and Shiawassee Rivers downstream of Greenpoint Island, as defined in the Hazardous Waste Management Facility Operating License, which was issued on June 12, 2003 by Michigan Department of Environmental Quality (MDEQ) to The Dow Chemical Company (Dow).

Previous documents have reported concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the sediments, floodplain soils, and fish of the Tittabawassee River that exceed some state generic criteria (Taylor et al., 2002, Hilsherova et al., 2003, MDEQ, 2003). As outlined in the Operating License, specific activities have to be undertaken. One of the requirements under the conditions of the Hazardous Waste Management Facility Operating License is that an ecological risk assessment (ERA) needs to be conducted as part of the Remedial Investigation (RI) process. As recognized by the USEPA (USEPA, 1997; USEPA 1998), site-specific field studies are almost always required for sound decision making. This is especially true for complex systems such as the Tittabawassee River.

Due to the results of previous investigations that demonstrated that some concentrations of PCDDs and PCDFs in the Tittabawassee River floodplain soils downstream of Midland are greater than those from reference locations (MDEQ, 2002, 2003; Hilsherova et al., 2003), questions have been raised regarding the risk of PCDD/Fs to wildlife that reside and/or forage within the Tittabawassee River and associated floodplains. Currently, there is minimal information on the presence or concentration of PCDDs and PCDFs in the tissues or diets of avian and mammalian wildlife species that reside within the Tittabawassee River and floodplain downstream of Midland, Michigan or from other locations that could be used as reference areas.

As a result, a more refined investigation is needed to reduce some of the uncertainties relative to species-specific dietary exposure concentrations and tissue residue concentrations in wildlife that are potentially exposed to PCDDs and PCDFs in the Tittabawassee River and floodplain soils. The Work Plan associated with this QAPP describes in detail a series of site-specific studies and sample collections to be performed by the Michigan State University Aquatic Toxicology Laboratory (MSU-ATL) of the Department of Zoology and National Food Safety and Toxicology Center (NFSTC). Supplemental investigations will be conducted by ENTRIX, Inc. as specified in this Work Plan. The ERA Work Plan will include detailed plans for evaluating the aquatic and terrestrial resources and food webs of the Tittabawassee River and floodplain. In addition, the RI will include a detailed description of the ecosystem including the identification of key plant and animal species.

2.2 Project Description

The studies presented in the Work Plan are designed to elucidate site-specific and congener-specific stressor exposure and population health for those ecological receptors previously identified as being of greatest priority. The studies are of two types: exposure studies and effects studies. Exposure studies will gather site-specific data on the concentrations of individual PCDD/F congeners. This will better define PCDD/F exposures, thereby minimizing the need for conservative exposure and effects assumptions. Studies on effects will examine receptor populations present at the "Site". Site-specific population health

studies were developed to provide the appropriate data where such data were lacking in the previous evaluations.

Effects of PCDD/Fs can be better predicted by integrating congener-specific exposures to congener-specific toxicities. There are 75 PCDD congeners and 135 PCDF congeners that vary in the degree and position of chlorine substitution. Of the 210 PCDD and PCDF congeners, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD, also referred to as TCDD) is considered to be the most potent and is the one most studied. For example, the potency of TCDD and related compounds in avian and mammalian wildlife has been well-established in laboratory and field studies (Murray et al., 1979; Gilbertson et al., 1991; Giesy et al., 1994; Ludwig et al.,1996; Tillitt et al., 1996; Powell et al., 1997). Observed effects of TCDD and related chemicals in wildlife and laboratory animals include biochemical adaptive changes such as enzyme induction, developmental deformities, reproductive failure, liver damage, wasting syndrome, and death. As a result, the biological effects of PCDD/Fs are highly congener-specific and are expressed primarily through the Ah-receptor pathway (Okey et al., 1994). As a result, PCDD/F toxicity can be assessed by converting congener-specific data to 'Toxic Equivalents' using appropriate Toxic Equivalency Factor values (Van den Berg et al.,1998).

Pesticide residues have also been detected in the tissues of some key receptors at the in the vicinity of the "Site". Most notably relatively great concentrations of DDT metabolite have been detected in the tissues of great horned owls found at the site. Therefore, residues of *p,p'*-DDT and its metabolites (*p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT) will also be monitored to evaluate the relative risks contributed by DDT.

2.2.1 Applicable Technical Quality Standards or Criteria

The study is being conducted to evaluate PCDD/Fs exposure in the environment. As such, there are no applicable regulatory or technical standards to which the analytical data will be compared. All analytical data will be collected under the QA/QC standards specified in the relevant analytical methods (EPA Method3 8290A 8270C and 1668A).

2.2.2 Special Personnel or Equipment Requirements

Special equipment requirements for the proposed work include, 3 Nexttel™ combination 2-way radio and digital cellular phones, a Wildco® sediment coring device and a surface sediment sampling device. Observational equipment includes 4, Bushnell spotting scopes, 12 portable blinds, 12 folding chairs and 4 propane heaters. Organism collection equipment may include an aquatic insect emergence trap, Ponar grab sampler, sweep nets, minnow traps, Smith Root 1.5 KVA stream electrofisher, AbP-3 backpack electrofisher, pitfall traps, bird boxes and platforms, and Sherman live traps to collect a variety of aquatic and terrestrial species. Personnel will be used that are trained to work and/or take measurements with this equipment and identify the variety of aquatic and terrestrial species encountered. Additional information on special training, requirements and certifications are presented in Section 2.6. Procedures for collection of organisms are specified in the applicable SOPs attached to the SAP. Field personnel will be equipped with suitable PDAs to facilitate the electronic collection of field data and permit the backup and transfer of that data to central storage.

2.2.3 Assessment Techniques

A summary of assessment activities that are required for the work are as follows:

- Assessment of field operations. To evaluate field operations performance, frequent review of sample collection documentation, COCs, field notebooks and field measurements, and the performance of unannounced field operation audits will be conducted.

- Assessment of laboratory operations. An audit of the MSU-ATL facility will be performed quarterly by the QA manager. All inspections of the study facilities will be unannounced. Laboratory audits will include assessments of all sample tracking and other documentation, instrument log books, personnel working on the project and their training records and a random audit trail check of selected samples. Any nonconformities will be reported to Mr. Patrick Bradley and the Project Director within five working days and official notification of corrective actions will be reported to the QA manager and Project Director within an additional five working days. If the QA manager determines that nonconformities are of a nature that would compromise sample integrity he will have authority to order immediate cessation of laboratory operations until corrective measures are in place and notified to the QA manager and project director.

Specific details of assessment procedures can be found in Section 4.0.

2.2.4 Work Schedule

Sampling and analysis are to begin in April 2004 and will continue through 2007. Data analysis and interpretation will continue through 2008.

2.2.5 Project and Quality Records and Reports

Critical records for this project include:

- field operations records;
- project reports outlined above; and
- laboratory records.

More details on project records and reports can be found in Section 2.6.

2.3 Data Quality Objectives and Criteria for Measurement Data

In this section the data quality objectives for the work tasks and the performance criteria and measurement system that will be employed are discussed.

2.3.1 DQO Development

Data quality objectives (DQOs) are both qualitative and quantitative statements that define the type, quality, and quantity of environmental data appropriate for the intended application. The DQO process used for this project follows the EPA QA/R-5 regulations (USEPA 1998) and EPA QA/G-4 guidance (USEPA 1994b). Quality assurance activities associated with all sampling and analysis are addressed in the SOPs for those activities. DQOs associated with field studies are addressed in the Sampling and Analysis Plan portion of the ERA Work Plan.

2.3.2 Method Performance Objectives

The sampling approach and rationale are presented in the Sampling and Analysis Plan and are discussed in terms of DQOs. Method performance requirements for analytical laboratory methods to be performed for the study are expressed in terms of precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS). Summarized below are brief definitions for each PARCCS parameter, with calculation equations as appropriate.

2.3.2.1 Precision

Precision is an estimate of the variability between individual measurements of the same physical or chemical property, under prescribed similar conditions.

Field Precision

Field precision is usually assessed through the collection and measurement of duplicate field samples at the same location. The duplicate sample is submitted "blind" to the laboratory, and sample results are compared to check for the overall variability introduced by sampling and analytical procedures. The field duplicate approach is generally not applicable to systems where the experimental unit is the single organism since each individual is represents a sampling replicate. Homogenizing of such an individual organism and preparation of replicate samples represents an analytical duplicate rather than a field duplicate. Similarly when a single soil sample is collected and divided into additional blind samples these replicate samples represent analytical replicates. However, if a composite soil sample is prepared by the compositing of numerous individual cores then a field duplicate can be prepared by collecting a second series of cores adjacent to the first. However, it should be noted that PCDD/F concentrations in soils are known to be highly variable spatially and so variability in field duplicated can be considerable. Another example of a field duplicate would be the collection of two samples of insects at the same location at the same time. However, these two samples cannot be generated by collection of a single composite and then splitting it into two samples. Therefore we will not determine field precision in these studies.

Laboratory Precision

Precision in the laboratory is assessed through the calculation of the relative percent difference (RPD) for two replicate samples. The precision of the analysis can be inferred through the use of one of the following: 1) laboratory control spike and laboratory control spike duplicate (LCS and LCSD) samples, which are laboratory blank samples spiked with known analyte concentrations, 2) matrix spike and matrix spike duplicate (MS/MSD) samples which are project samples spiked with known analyte concentrations, or 3) duplicate analyses of unspiked project samples. The laboratory analyzes one or more of the aforementioned types of duplicate samples at a rate of one per batch of twenty (20) or fewer investigative samples per matrix.

The MS/MSD samples provide information about the effect of the sample matrix on extraction and measurement methodology. An MS/MSD pair will be analyzed at a rate of one per twenty (20) per analytical batch or fewer investigative samples per matrix.

Calculating the RPD for each pair of duplicate analyses (e.g., MS/MSD, laboratory control sample spike duplicates, unspiked duplicate samples) and the RPD for field duplicate sets, using the following formula will assess the precision of laboratory analyses:

Equation 2-1

$$RPD = \frac{S - D}{(S + D)/2} x100$$

where:

RPD = Relative Percent Difference, %.

S = First sample value (original or MS value or larger of the duplicate),

D = Second sample value (duplicate or MSD value or smaller of the duplicate),

2.3.2.2 Accuracy

Accuracy is the degree of agreement between a measurement or observation and an accepted value.

Field Accuracy

Accuracy in the field is assessed through the collection and analysis of appropriate field equipment blanks and trip blanks, and achieved through adherence to all sample handling, preservation, and holding time requirements. Field blank samples are analyzed to check for procedural contamination that may cause sample contamination. Equipment rinse blanks are used to assess the adequacy of decontamination of sampling equipment between collection of individual samples. Trip blanks are used to assess the potential for contamination of samples due to contaminant (i.e., volatile organic compounds) migration during sample shipment, handling, and storage. Accuracy of the field instruments will be assessed by using daily instrument calibration and calibration checks. Field blank, equipment rinsate blank, and trip blank analysis frequencies are given in Table 2-1.

Laboratory Accuracy

Laboratory accuracy is assessed by the analysis of method blanks, surrogate spikes, matrix spikes (MS), laboratory control samples (LCS), and/or Standard/Certified Reference Materials (SRM). The results are expressed as percent recovery. Method blank samples are generated within the laboratory and used to assess contamination resulting from laboratory procedures. Surrogate compounds are used in analyses for organic contaminants and specified in the analytical method. Prior to sample extraction, surrogate compounds are added to each organic environmental, blank, spike, and duplicate sample. Method blanks, MS, LCS, and/or SRM samples will be analyzed at a rate of one per analytical batch of twenty (20) or fewer investigative samples/matrix.

The percent recovery (percent R) of spike samples will be calculated using the formula:

Equation 2-2

$$R = \frac{A - B}{C} x100$$

where:

R = Recovery, %

A = The analyte concentration determined experimentally from the spiked sample, units.

B = The background level determined by a separate analysis of the unspiked sample, units.

C = The amount of the spike added, units.

Table 2-1. Field QC Samples for Precision and Accuracy.

Type of QC Sample	Frequency	Acceptance Criteria
Equipment rinsate blank	2 per day per equipment type	No analyte should be detected at >3 times the laboratory blank
Matrix spike/matrix spike duplicate (MS/MSD)	1 per 20 tissue samples	RPD should be ≤30 % for each analyte.
Field blank	1 per day	No analyte should be detected at >3 times the laboratory blank.

Note: MS/MSD samples are included as field QC samples for planning purposes, to ensure sufficient sample volume is collected for the analyses.

2.3.2.3 Representativeness

Representativeness is a qualitative measure of the degree to which sample data accurately and precisely represent a characteristic environmental condition. Representativeness is a subjective parameter and is used to evaluate the efficacy of the sampling plan design. Representativeness is demonstrated by providing full descriptions of the sampling techniques and the rationale used for selecting certain tissue samples and sampling locations in the project planning documents.

There cannot be a target numerical goal for a qualitative parameter such as representativeness or comparability. Therefore, this criterion is completed and evaluated subjectively rather than quantitatively. The measure for representativeness is answered during the preparation of the sampling and analysis approach and rationale, and then reassessed during the data usability process. For example, an integral part of developing the sampling and analysis approach and rationale is to answer the question "How many samples are needed to fully evaluate x?" Then, during the data usability process, the question "Were enough data collected to answer the original question?" must be answered. Thus, it is not possible to construct a table with numerical goals that can be used to evaluate these subjective measures. The criteria to make these decisions can be based on power analysis conducted after initial information has been collected or during data interpretation to determine if additional samples are necessary to fully describe the nature and extent.

Since the analytical samples will generally be obtained as homogenized tissue composites from individual specimens an assessment of the representativeness of the homogenized samples is required. Sample homogenates will be prepared as composite samples containing standardized amounts of collected tissues. To ensure complete homogenization of the samples, duplicate aliquots of 10% of samples will be submitted to the analytical laboratories as blind replicates.

2.3.2.4 Comparability

Comparability expresses the confidence with which one data set can be compared with another data set obtained during parallel or previous investigations. Comparability can be related to precision and accuracy, since these parameters are measures of data reliability.

Results of chemical analyses in the same medium are generally considered comparable if the same procedures for collecting and analyzing the samples are employed, if the samples comply with the same QA/QC procedures, and if the units of measurements are the same.

Only some of the tissue types to be collected for analysis for this study have not been collected from the Tittabawassee River previously. Where appropriate results for samples from the current study will be compared to results from previously collected samples to determine comparability.

The analytical protocols for PCDD/F determination for this study will be comparable with previous data collected for fish in the river (Hilscherova et al. 2003; ENTRIX 2004). The method used, based on US-EPA method 8290, determines each PCDD/F congener individually so data will be amenable to comparison with other PCDD/F determinations. The acceptability criteria for the method are performance based and compliance with QA/QC requirements will be ensured.

The quality objectives for data from each field sampling and analysis task within this study is to achieve a level of comparability that allows for the comparison of data collected among all field tasks for this study. To accomplish this goal, all data generated during the tasks included in this investigation will be subject to strict QA/QC procedures as specified in this QAPP.

2.3.2.5 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was planned to be obtained under normal conditions. Data completeness will be calculated by using Equation 2-3.

Equation 2-3

$$\%\ \text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \text{x} 100$$

Experience on similar projects has shown a reasonable goal considering combined historical field and laboratory performance is 90 percent completeness. All valid data will be used. During the data validation process, an assessment will be made of whether the valid data are sufficient to meet project objectives. If sufficient valid data are not obtained, the Project Manager will initiate corrective action. Where invalid data is generated all documentation and the reasons for the invalidation of the data will be provided.

2.3.2.6 Sensitivity

Sensitivity is the measure of the concentration at which an analytical method can positively identify and report analytical results. The sensitivity of a given method is commonly referred to as the detection limit. Although there is no single definition of this term, the following terms and definitions of detection limits will be used for this program.

- **Instrument detection limit** (IDL) is the minimum mass of analyte that can be measured above instrument background noise under ideal conditions.
- **Detection limit** (MDL) For GC/MS analysis detection limits are generally first determined as a sample-specific estimated detection limit (EDL). The EDL is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. The EDL is then used in conjunction with information about the amount of sample used and amount of surrogates added to calculate a sample specific MDL.

The sum TEQ for all MDLs in a single sample may not exceed 0.9 pg TEQ/g. Table 2-2 gives target ranges for congener specific MDLs. These limits are of sufficient sensitivity to allow for comparison to toxicological benchmarks. The MDL for each congener is a function of signal to noise ratio for each sample, which affects the amount of compound detectably different from baseline, and the sample mass used. An MDL is also provided based on the calculation of "total dioxin equivalents" based on the WHO promulgated TEF values for various animal classes (van den Berg et al. 1998).

Sample MDLs will vary from sample to sample and will depend on the amount of samples processed. Failure of the analytical laboratory to achieve the required MDLs will impair the ability to statistically compare sampling locations.

Table 2-2. PCDD/F Congeners to be analyzed and target MDLs

Compound	CAS No	Target MDL (pg/g)*
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	1746-01-6	0.1-1
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	40321-76-4	0.1-1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	57653-85-7	0.1-1
1,2,3,4,7,8- Hexachlorodibenzo-p-dioxin (HxCDD)	39227-28-6	0.1-1
1,2,3,7,8,9- Hexachlorodibenzo-p-dioxin (HxCDD)	19408-74-3	0.1-1
1,2,3,4,6,7,8- Heptachlorodibenzo-p-dioxin (HpCDD)	35822-39-4	0.1-1
Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	1-5
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9	0.1-1
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6	0.1-1
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4	0.1-1
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9	0.1-1
1,2,3,7,8,9- Hexachlorodibenzofuran (HxCDF)	72918-21-9	0.1-1
1,2,3,4,7,8- Hexachlorodibenzofuran (HxCDF)	70648-26-9	0.1-1
2,3,4,6,7,8- Hexachlorodibenzofuran (HxCDF)	60851-34-5	0.1-1
1,2,3,4,6,7,8- Heptachlorodibenzofuran (HpCDF)	67562-39-4	0.1-1
1,2,3,4,7,8,9- Heptachlorodibenzofuran (HpCDF)	55673-89-7	0.1-1
Octachlorodibenzofuran (OCDF)	39001-02-0	0.1-1
SUM WHO-TEQ MUST NOT EXCEED 0.9 pg/g (ww)		

* Units represent wet wt for tissues.

2.4 Laboratory Comparison

To ensure timely, accurate and independently verifiable results for this study, two primary analytical facilities have been selected (see Section 3.1.2). To ensure the validity and comparability of results from the two laboratories, a program of blind sample replicates will be used to provide data for intra- and inter-laboratory comparison.
Quality assurance criteria for acceptability and usability of data are provided in Table 3-3 of this QAPP.

2.5 Special Training, Requirements, and Certifications

The Project Manager is responsible for assembling a project team with the necessary experience and technical skills. Part of the process is to identify special training requirements or certifications necessary to execute the project successfully. Project-specific requirements include training specific to the analytical methods to be conducted, specific collection and handling methods for tissue samples, and health and safety training for field and laboratory activities.

All field personnel will receive training before commencing fieldwork to ensure they are familiar with the required SOPs and are adequately skilled at sample and field data collection. Personnel training records are maintained by the laboratory manager.

Additionally, all contractors working at the site should have the appropriate health and safety training as outlined in the Health and Safety Plan.

The analytical laboratories chosen for the study both have extensive experience and certification for the determination of PCDD/Fs in a wide variety of matrices. Both laboratories are recognized as world leaders in this field of analysis.

2.6 Documentation and Records

This section identifies critical field and laboratory records required for this project, information to be included in project reports, the data reporting format for analytical data report packages, and the document control procedures to be used.

2.6.1 Required Records

The critical records required for this project are identified below with descriptive or supporting information as appropriate. Records information is presented below for field operations. Critical laboratory records are described in Section 2.7.3 of this QAPP.

Critical records generated during field operations are listed below.

- Sample collection records including field notebooks, photographs, and any other records used to record raw data. General field procedures will be referenced in the field notes, while any necessary deviations or modifications required to collect samples will be described in detail.
- Chain-of-custody records (COC).
- Field QC sample records.
- Corrective action reports.

The information contained in these records documents the overall field operations. Procedures for field operations records control, archiving, and storage are described in Section 2.7.4 of this QAPP.

2.6.2 Project Reports

Several types of reports will be produced during the course of this project. The Project Manager will prepare summary reports for investigations described herein. Tasks described herein will be submitted in the following technical report publications and manuscripts to be submitted to the peer-reviewed scientific literature, including summary report of data and QA determinations.

2.6.3 Laboratory Records

All analytical results for tissue data will be reported in an approved format, described below. In addition to the reported data, the laboratory data report will, at a minimum, include a narrative that will discuss any problems or discrepancies, and sufficient calibration and QC information to determine that the method was in control at the time that the samples were analyzed. The laboratory records will include:

- Case narrative;
- COC documentation (external);

- Laboratory sample ID, field sample ID, location, matrix, and dilution factors;
- Sample receipt, extraction, and analysis dates for holding time verification;
- Percent recovery of each surrogate;
- Final analyte concentration including reporting limit, laboratory qualifiers, and re-analyses;
- Surrogate recovery control limits;
- Percent recovery of each compound in the MS sample;
- MS recovery control limits;
- RPD for all MS/MSD and/or LCS/LCSD results;
- RPD control limits for MS/MSD and/or LCS/LCSD reports;
- Laboratory control sample results when analyzed;
- Recovery control limits for LCS or SRM recoveries and RSD;
- Blank results for method blanks, field blanks, equipment blanks, and trip blanks; and
- Method blank summary indicating associated samples.

For data validation, the following additional data will be required:

- Sample receipt/sample log-in forms;
- Calibration information, including initial calibration, concentration response data of the calibration check standards, continuing calibration check data, instrument tunes, and associated samples;
- Internal standard areas and retention times; and
- All raw data and logs will include the following information:
    - analyst's initials and date
    - initial and final sample and extract volumes or weights and/or dilutions
    - condition of instrument (e.g., retention times for GC)
    - documentation linking sample analysis to instrument calibration (where appropriate)
    - time of start of analysis of all field and QC samples
    - instrument run log showing analytical sequence
    - dilutions performed and amount of sample analyzed or injected
    - field samples, QC samples, and blanks clearly labeled
    - chromatograms and quantitation reports
    - sample preservation (where applicable)

In addition to the hard-copy report requirements, the laboratory will provide (1) electronic deliverables conforming to an ASCII comma-delimited format for all data reported and (2) an electronic back up for all laboratory data generated.

Procedures for project control, archiving, and storage of laboratory records are described in Section 2.6.4 of this QAPP. The laboratory's internal records management protocols are described in SOP #802 (Appendix H) entitled, "Data Package Review". MSU-ATL and ENTRIX, Inc. will adhere to a record retention time (RRT) of 7 years for all laboratory records for the project.

2.6.4 Record Maintenance and Storage

All documents relating to the project will be controlled to assure proper distribution, filing, and retrieval, and to assure that revisions are properly recorded, distributed, and filed.

Project records will be stored and maintained by ENTRIX, Inc. The Project Manager and office staff are responsible for organizing, storing, and cataloging all project information and for collecting records and supporting data from project team members. Once cataloged, ENTRIX will assure that project records are appropriately filed by category in the correct project file. Filed documents are available to MSU-ATL and ENTRIX staff through check-out procedures developed to assure the integrity of the project file. Individual project team members may maintain separate files or notebooks for individual tasks. These files or notebooks are transferred to the project manager as part of project close-out. The archived files will be stored and maintained by ENTRIX, Inc. Additional information on record management can be found in Section 3.9.7 and 3.9.8 of this QAPP.

3.0 MEASUREMENT AND DATA ACQUISITION

This section describes all aspects of measurement design and implementation, and discusses the methods that will be used for sampling, analysis, data handling, and QC in support of the tasks discussed herein. The following specific aspects of measurement and data acquisition will be covered in this section:

- Sampling process design;
- Sampling methods requirements;
- Sample handling and custody requirements;
- Analytical method requirements;
- Quality control requirements;
- Instrument/equipment testing, inspection, and maintenance requirements;
- Instrument calibration and frequency;
- Inspection and acceptance requirements for supplies and consumables;
- Data acquisition requirements; and
- Data management.

3.1 Sampling Process Design

The measurements to be taken and the media to be sampled include concentrations of PCDD/F congeners in various tissues of biota and environmental matrices.

The planned sampling locations and rationale for selection are detailed in the Sampling and Analysis Plan (SAP). Any modifications to the work tasks described therein will be presented as an addendum or update to the SAP.

3.1.1 Field Sampling Documentation

Field team members will maintain bound field logbooks to provide a daily record of significant events, observations, and measurements during sampling. Each data book will have a unique identifier and each page and carbon copy will include this data book identifier. All information pertinent to sampling will be recorded in the logbooks. Each day's logbook entries will be signed and dated and will include:

- Name and title of author, date and time of entry, and weather and environmental conditions during the field activity;
- Location of sampling activity;
- Sampled species or environmental matrix;
- Sample collection method; and
- Number of samples taken.

When activity-specific data forms are used, they will also include:

- Project name and number;
- Investigation location;
- Sampler's initials;
- Sampled species; and
- Sample collection method.

The following information will be recorded either in the logbook or on the activity-specific data forms:

- Date and time of collection;
- Sample identification number(s);
- Sample destination (e.g., laboratory);
- Field observations;
- Field measurements; and
- Sample handling (preservation).

All original data recorded in field logbooks, field data forms, sample labels, and COC forms must be written with waterproof, indelible ink. None of these accountable, serialized documents are to be destroyed or discarded, even if one is illegible or contains inaccuracies requiring document replacement. If an error is made on an accountable document assigned to one individual, that individual will make all corrections simply by crossing a line through the error, initialing and dating the correction, and entering the correct information. The erroneous information will not be obliterated. The person who made the entry will correct any subsequent error discovered on an accountable document. All personnel will be trained in the proper use of notebooks during training for field work.

During the course of this study ATL will undertake to enter data into a Personal Digital Assistant (PDA) system to aid in automation of data collation and upload. Procedures and systems for the entry, verification, backup and compilation are currently underway. Until these systems and procedures are in place and ATL can verify the integrity and security of such data the hardcopy paper records discussed above will be kept. All PDA entered data records will contain the same information as the paper records. When PDA data entry is implemented it will be the responsibility of Dr Denise Kay (ENTRIX) to ensure that suitable electronic and/or paper copies of all PDA data are prepared and transferred to the security of the project archive.

3.1.2 Sample Identification

The field analysis and sample identity information are recorded in bound field logbooks or recorded on data sheets while in the custody of the sampling team.

A sample label will be completed and attached to each animal and sample container for every species collected. Labels consist of a waterproof material backed with a water-resistant adhesive. Labels are to be filled out using waterproof ink, and are to contain at least the following information:

- Sampling date and time;
- Sample identification number;
- Investigation location;

- Sampler's initials;
- Sample matrix or matrix identifier.

Each sample to be analyzed for residues will be assigned a unique number consisting of an alphanumeric code that identifies the investigative area, medium (tissue), and the specific sampling location. These numbers will be tracked electronically, from collection through laboratory analysis and into the final reports.

The sample number will be cross-referenced with the site name and sample location on the COC. Additional sample volume will be collected for samples identified for laboratory QC purposes (i.e., MS, MSD, DUP) and identified as "For Lab QC Use." Information to be included on COCs is specified in SOP TR401 entitled, "Sample Management - Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal".

3.1.2.1 Tissue Sample Handling Procedures

Appropriate sample containers will be sealed, labeled, and placed on wet or blue ice in an insulated container. Appropriate COC documentation will accompany the samples as required by the QAPP. Specific sample volumes, sample containers, preservatives, and replication of samples are detailed in the following sections. Any sampling equipment that will be reused will be decontaminated by rinsing with deionized water followed by reagent grade acetone and hexane between sampling.

3.1.2.2 Decontamination Procedures and Materials

All equipment used during investigation activities that could come into contact with chemically affected materials will be thoroughly cleaned, before and after each use, by washing with Liquinox (a laboratory-grade detergent) and rinsing with deionized water followed by reagent grade acetone and hexane. Decontamination procedures may be modified and/or revised based upon the data obtained or the field equipment used.

Decontamination waste is expected to consist of acetone and hexane. Decontamination solutions will first be discharged to drums in a designated staging area and then later transferred to laboratory facilities for proper disposal and management.

3.1.3 Support Facilities for Sampling Methods

The primary laboratories for analysis of samples collected for this study will be:

- MSU-ATL Analytical Chemistry Laboratory, Michigan State University, East Lansing, MI 48824.
- AgriQuality Limited, 1B Bell Road, PO Box 31-242, Lower Hutt, New Zealand.

3.1.4 Sampling/Measurement Failure Response

If QC surveillance and/or field audits result in detection of unacceptable conditions, procedures or data, the Project Manager, in conjunction with the QA Manager, will be responsible for developing and directing implementation of corrective actions. Corrective actions will include one or more of the following:

- Identifying the root cause of the problem and implementing systems to prevent future occurrences;

- Identifying the source of the violation;
- Evaluating and amending sampling and/or analytical procedures; and
- Accepting data and flagging the data to indicate the level of uncertainty associated with failure to meet the specified QC performance criteria.

Any finding requiring corrective action must be documented to the Project Manager. The Project QA Manager will check to ensure that corrective actions have been implemented and that the problem has been resolved. Problems will be addressed and the corrective action noted in the appropriate lab or field notebook.

If an error is made on an accountable document assigned to one individual, that individual will make all corrections simply by crossing a line through the error, initialing and dating the correction, and entering the correct information. The erroneous information will not be obliterated. The person who made the entry will correct any subsequent error discovered on an accountable document.

3.1.5 Sample Preservation and Holding Time Requirements

The sample containers, preservative requirements, and maximum holding times for analytical methods used in this project are provided in Table 3-1.

Table 3-1. Required Sample Containers, Preservation, and Holding Times.

Analyses	Sample matrix[a]	Container[b]	Preservative[c]	Holding time[d]
PCDD/F congeners (EPA Method 8290, Sec. 6.4)	S, P, T	125ml Glass	Freeze -20°C	365 days
PCB congeners (EPA Method 1668, Sec. 8.5)	S, P, T	125ml Glass	Freeze -20°C	365 days
DDT compounds (EPA Method 8270C)	S, P, T	125ml Glass	Freeze -20°C	Not specified
Percent Lipids (gravimetric)	S, P, T	N/A	Freeze -20°C	NA

Note:
Sample container and volume requirements will be specified by the analytical laboratory performing the tests. Three times the required volume should be collected for samples designated as MS/MSD samples.

[a] Sample matrix: T = Tissue

[b] Glass containers will be pre-cleaned and sealed with Teflon®-lined screw caps and solvent rinsed foil.

[c] Tissue samples will be shipped at 4°C to the laboratory and stored at -20°C after dissection/processing.

[d] Holding times are from the time of sample collection. Holding times are based on method 8290. All extracts will be analyzed within 45 days of extraction. Numbers represent days to analysis of extract.

3.2 Sample Handling and Chain of Custody Requirements

Proper sample handling, shipment, and maintenance of chain of custody (COC) are key components of building the documentation and support for data that can be used to make program decisions. It is essential that all sample handling and sample COC requirements be performed in a complete, accurate, and consistent manner. Sample handling and custody requirements must be followed for all samples collected as part of this project.

3.2.1 Sample Custody

Sample custody and documentation procedures described herein must be followed throughout all sample collection activities. Components of sample custody procedures include the use of field logbooks, sample labels, custody seals, and COC forms. The COC form must accompany the samples during shipment from the field to the laboratory.

A sample is under custody under the following conditions:

- It is in one's actual possession;
- It is in one's view, after being in his or her physical possession;
- It was in one's physical possession and that person then locked it up to prevent tampering; and/or
- It is in a designated and identified secure area.

The following procedures must be used to document, establish, and maintain custody of field samples:

- A sample label will be completed and attached to each sample container for every sample collected. Labels consist of a waterproof material backed with a water-resistant adhesive. Labels are to be filled out using waterproof ink, making sure that the labels are legible and affixed firmly on the sample container. Sample labels are to contain at least the following information: sampling date and time; sample identification number; investigation location; and sampler's initials.
- All sample-related information must be recorded in the project logbook or on activity-specific data forms.
- The field sampler must retain custody of samples until they are transferred or properly dispatched.
- To simplify the COC record and minimize potential problems, as few people as possible should handle the samples or physical evidence. For this reason, one individual from the field sampling team should be designated as the responsible individual for all sample transfer activities. This field investigator will be responsible for the care and custody of the samples until they are properly transferred to another person or facility.
- A COC record will accompany all samples. This record documents the transfer of custody of samples from the field investigator to another person, to the laboratory, or other organizational entities, as a signature for relinquishment and receipt of the samples must accompany each change of possession. Chain-of-custody will be prepared for groups of samples collected at a given location on a given day.
- The COC form makes provision for documenting sample integrity and the identity of any persons involved in sample transfer. Information entered on the COC will consist of the following:
    - project name and number;
    - field logbook number;
    - chain-of-custody serial number;
    - project location;
    - sample numbers;
    - sampler/recorder's signature;
    - date and time of collection of each sample;
    - collection location;
    - sample type;
    - analyses requested;

- inclusive dates of possession;
- name of person receiving the sample;
- laboratory sample number;
- date of receipt of sample;
- name, address, and telephone number of laboratory;
- name, address, and telephone number of person to whom laboratory report will be sent; and
- method of delivery and courier.

- Completed COC forms will be inserted into a Ziploc™ bag, sealed, and taped to the inside cover of the shipping container used for sample transport from the field to the laboratory when a courier or shipping company is used. The shipping company will not sign for custody of the samples.
- When samples are relinquished to a courier for transport, the tracking number from the shipping bill or receipt will be recorded on the COC form or in the site logbook.
- The recipient for the samples must be notified of the date of shipment and anticipated time of arrival. The shipping bill number must also be provided to the recipient to enable tracking of samples.
- It must be clearly established prior to shipment who will be responsible for ensuring that timely sample delivery occurs and who will track the samples in case of shipping delays.
- The recipient of the samples must inform the sender when the samples are delivered.
- Custody seals must be affixed on shipping containers when samples are shipped to the laboratory to prevent sample tampering during transportation.
- In cases of delivery delay or packing damage all details of damage and sample condition must be recorded and if necessary photographed for documentation.

3.2.1.1 Laboratory Sample Handling and Custody

The Project Liaison or Field Team Leader (FTL) will notify the Laboratory Project Manager of upcoming field sampling activities and the subsequent transfer of samples to the laboratory. This notification will include information concerning the number and type of samples to be shipped, analyses requested, and the expected date of arrival. The Laboratory Project Manager will notify appropriate laboratory personnel about the expected shipment including the sample custodian.

Upon arrival at the laboratory, the samples will be received and logged in by a trained sample custodian in accordance with the laboratory's sample handling program. A description of the laboratory's general program is provided in SOP TR401 and is summarized below.

Upon sample receipt, the sample custodian is responsible for performing the following activities during sample receipt where appropriate:

- Examining the shipping containers to verify custody seals, if used, are intact;
- Examining all sample containers for damage;

- Take digital photographs of any custody seals used, before opening, and of any damage to the shipping container or individual sample containers
- Comparing samples received against those listed on the COC;
- Verifying sample holding times have not been exceeded;
- Determining sample temperature (from the temperature blank vial) and documenting variations from the acceptable range on the COC;
- Verifying that all samples listed on the COC are present or accounted for;
- Immediately signing and dating COC after shipment is accepted;
- Noting any sample receipt problems on the COC, initiating a Condition Upon Receipt report (CUR), and notifying the Laboratory Project Manager;
- Attaching laboratory sample container labels with laboratory identification number and test; and
- Placing the samples in proper laboratory storage.

The Laboratory Project Manager is responsible for contacting the Project Liaison as soon as possible if any problems are identified during sample receipt. All identified sample receiving problems will be resolved before sample preparation and analysis.

Following sample receipt, the sample custodian is responsible for logging the samples in the laboratory sample log-in book, and/or the Laboratory Information Management System (LIMS) with the following information:

- Laboratory project number;
- Sample numbers (laboratory and client);
- Type of samples;
- Required tests;
- Date collected; and
- Date received.

The sample custodian is also responsible for notifying the Laboratory Project Manager and appropriate Group/Team Leader(s) of sample arrival and placing completed COCs, waybills, and any additional documentation in the project file.

Samples will be stored appropriately within the laboratory to maintain any prescribed temperature, to protect against contamination, and to maintain the security of the samples.

If any samples are transferred to a different laboratory, the transfer will be done under COC procedures and ENTRIX will maintain the appropriate documentation to preserve the traceability of the samples through final analysis and disposal.

3.2.2 Sample Packing and Shipping

Samples will be delivered to the designated laboratories by field personnel, laboratory courier, or by commercial shipping services (such as UPS or Federal Express). The method of sample shipment will be noted on the COC. During the field effort, the FTL or a designee will inform the laboratory daily of

planned shipments. Hard plastic ice chests or coolers with similar durability will be used for shipping samples. The coolers must be able to withstand a 4-foot drop onto solid concrete in the position most likely to cause damage. The samples will be packed to prevent the least amount of damage if such a fall would occur.

After packing is complete, the cooler will be taped shut with custody seals affixed across the top and bottom joints. Each container will be clearly marked with a sticker containing the originator's address.

The following procedures must be used when transferring samples for shipment.

- A COC form must accompany samples. When transferring possession of samples, the individuals relinquishing and receiving must sign, date, and note the time on the record. This record documents transfer of custody of samples from the field sampler to another person or to the laboratory. Overnight shipping companies will not be required to sign the COC. A copy of the receipt of shipment will accompany the COC.
- Samples must be properly packaged for shipment and dispatched to the appropriate laboratory for analysis with a separate signed COC form enclosed in each sample box or cooler. The COC should reflect only the contents of the cooler in which it is enclosed.
- A COC form identifying the contents must accompany all packages. The original record must accompany the shipment, and the FTL must retain a copy.

3.3 Analytical Methods Requirements

This subsection presents the analytical methods requirements for analyses that may be performed during the study including preparation/extraction procedures where appropriate and method performance requirements.

Michigan State University Aquatic Toxicology Laboratory and Agriquality will conduct laboratory analyses. The laboratory's QA protocols will be available in the project files and will contain summary information from the analytical methods including the following:

- Sample containers, preservatives, and holding times;
- Calibration requirements including frequency and acceptance criteria;
- Laboratory quality control samples including frequency, acceptance criteria, and corrective action; and
- MDLs.

More detailed information on the laboratory's analytical methods is presented in laboratory-specific SOPs that can be obtained directly from MSU-ATL and AgriQuality.

3.3.1 Analytical Methods

Analyses on this project will utilize EPA-approved methods, method 8290 will be used for the analysis of PCDDF congeners by HRGC/HRMS. As indicated in the SAP a portion of the samples will also be analyzed for PCB congeners using EPA method 1668A and for DDT compounds using EPA method 8270C. Method references for these analytical methods are provided in Table 3-2 including preparation/extraction methods where appropriate.

Table 3-2. Analytical Requirements for PCDD/F Methods.

Analyses	Preparatory Method[a]	Analytical Method	Reference
PCDD/F congeners	TR213	EPA method 8290A	http://www.epa.gov/epaoswer/hazwaste/test/main.html
PCB congeners	TR215	EPA method 1668A	http://www.epa.gov/Region3/1668a.pdf
DDT	TR205	EPA method 8270C	http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf

[a] Due to ongoing revision process for SOPs specific SOP version numbers are not provided here.

3.3.2 Reporting Limits

Target MDLs for the analysis of PCDD/F congeners are identified in Table 3-3 and are presented in Table 2-1. These MDLs are target values based on data quality requirements for the risk assessment of complex PCDD/F mixtures. These MDL may be modified based upon laboratory performance, sample matrix effects and/or changes to the methods. Any such modifications will be discussed with all stakeholders and any effects on the quality of subsequent risk assessment procedures will be determined.

3.3.3 Laboratory Method Performance Requirements

Summary tables of method-specific quality control samples that the laboratory uses to monitor method performance are specified in Method 8290. Acceptance criteria may be modified based upon the laboratory's current performance and/or changes to the methods. For each analysis, these tables present the types of QC samples to be run including the frequency, acceptance criteria and purpose of QC analysis. The laboratory analyst will review results of the quality control samples against the acceptance criteria. Any identified discrepancies will trigger the laboratory's internal corrective action system as described below.

Table 3-3. QC Samples and Acceptance Criteria for PCDD/F Congener Analysis

QA/QC Test	Acceptance Criteria	Frequency	Reason for Test
Retention time for Calibration Mix	value ±0.5min of mean	Daily	GC Performance
GC Linearity	PRRF CV ±3%	Weekly	Data Integrity
CRM/IRL	value ±20% of expected	1 per analytical set (20 samples)	Method Validation Representativeness and Comparability
Surrogate Recovery	value ±30% spiked concentration	for each sample extracted	Method Efficiency Data correction
Matrix Spike	value ±30% spiked concentration	1 per analytical set (20 samples)	Method Accuracy Representativeness and Comparability
Field Blank	concentration <IDL for first blank	1 per analytical set	Background Check; Complete Sampling System
Laboratory Blank	Should be < MDL, if present then MDL = concentration	1 per analytical set	Quality assurance (monitor laboratory contamination)
Field / Matrix spike Duplicate	RPD < 30%	1 per analytical set	Sampling Precision
Blind Check Sample	value ±30% expected value	Minimum of 1 during course of program	Method Validation; Representativeness and Comparability
Completeness	90% of Field Samples meet QA/QC	Evaluated at end of program	Project Integrity

3.3.4 Laboratory Corrective Action

Both laboratories have formal corrective action systems in place to assure that prompt action is taken when an unplanned deviation from a procedure or plan occurs and that whenever possible, corrective actions include measures to prevent the reoccurrence of deviations. Specific corrective actions will be taken and documented when a QC sample does not meet acceptance criteria. Following is a description of how information from the laboratory's corrective action system is communicated to the project team.

Corrective action procedures include prompt notification of the project contact (QA Manager) for any significant problems or discrepancies. The Laboratory Project Manager is responsible for reporting any significant problems or discrepancies that occur as analyses are conducted to the Project Liaison or other identified project contact. The Laboratory Project Manager is also responsible for assuring that corrective action is taken where appropriate to prevent the reoccurrence of similar problems or discrepancies. In addition, each analytical data report will include a case narrative that discusses any problems or discrepancies, and sufficient calibration and QC information to verify that the method was in control at the time that the samples were analyzed. The case narrative will also include a discussion of any corrective action taken by the laboratory to prevent the reoccurrence of similar problems or discrepancies.

3.4 Quality Control Requirements

This section presents the field QC checks that will be performed during field investigations including a discussion of field QC samples with frequency and acceptance criteria and field corrective action procedures. A discussion of laboratory QC samples is presented in Section 3.4.3 and laboratory corrective action is presented in Section 3.4.4.

3.4.1 Field QC Samples

The type and frequency of field QC samples to be collected during field investigations are summarized in Table 2-1 and are described below:

3.4.1.1 Equipment Rinsate Blank Samples

Equipment rinsate blanks (ERB) are samples of hexane passed through and over the surface of decontaminated sampling equipment. The rinsate is collected in sample bottles, preserved, and handled in the same manner as the samples. ERBs are used to monitor effectiveness of the decontamination process. The planned frequency for ERBs is one per day per equipment type. If more than one type of equipment is used to collect samples for a particular matrix, then an ERB is collected and submitted for each representative group of equipment. Typically, ERBs are analyzed for the same analytes as the corresponding samples collected that day.

3.4.1.2 Field (Trip) Blanks

Field blanks are unopened sample containers which are transported to and returned from the field collection location. Typically, at least one field blank per lot number of collected samples will be analyzed.

3.4.1.3 Duplicate (Blind) Field Samples

"Blind" duplicate field samples are collected to monitor the precision of the field sampling process. The use of field replicates to assess precision is discussed in section 2.4.2.1. Where appropriate field duplicates will be collected and submitted to the laboratories for analysis. Due to the constraints imparted by the selection of the experimental unit (e.g. individual animals) for some matrices, field duplicates cannot be analyzed for some matrix types.

3.4.1.4 Independent Confirmation of Results

To permit validation of data determined by MSU and AgriQuality, sample splits will be provided to Dow Chemical. A section of the final report will provide a comparison of data derived at the three laboratories.

3.4.2 Field Corrective Action

Problems that require corrective action may be encountered in the field. Any finding requiring corrective action must be documented to the Project Manager. The Project QA Manager will check to ensure that corrective actions have been implemented and that the problem has been resolved. More easily addressed problems may also be encountered in the field. Such problems will be addressed and the corrective action noted in the appropriate field notebook. If an error is made on an accountable document assigned to one individual, that individual will make all corrections simply by crossing a line through the error, initialing and dating the correction, and entering the correct information. The erroneous information will not be obliterated.

3.5 Equipment Inspection, and Maintenance Requirements

Maintenance and inspection of both field and laboratory equipment are described in the following sections.

3.5.1 Field Instrument/Equipment

Preventative maintenance of field instrumentation and equipment will be performed according to manufacturer's instructions. The field staff is responsible for ensuring that all instrumentation is operating properly prior to use. If problems are encountered, they will be documented in a bound field notebook. The faulty instrumentation/equipment will be scheduled for repair and sequestered and tagged until repaired and qualified for re-use.

3.5.2 Laboratory Instrument/Equipment

Laboratory instrument/equipment testing, inspection, and maintenance will be conducted in accordance with the procedures specified in the analytical laboratory QA manuals. The QA manual discusses the schedule, procedures, criteria, and documentation in place at the laboratory to prevent instrument and equipment failure and to minimize downtime. For each instrument or piece of equipment the laboratory maintains the following:

- Instrument/equipment inventory list;
- Instrument/equipment major spare parts list or inventory;
- External vendor service agreements (if applicable); and
- Instrument-specific preventive maintenance logbook or file.

The laboratory documents all preventive maintenance and repair for each instrument or piece of equipment in dedicated logbooks or files.

3.6 Instrument Calibration and Frequency

Calibration and frequency of calibration of both field and laboratory equipment are described in the following sections.

3.6.1 Field Instruments

The field equipment that will need calibration are listed below:

- GPS receiver
- Balance

Proper maintenance, calibration, and operation of each instrument will be the responsibility of field personnel assigned to a particular field activity. All instruments and equipment used during the field investigations will be maintained, calibrated, and operated according to the manufacturer's guidelines and recommendations.

3.6.2 Laboratory Equipment and Instrumentation

All laboratory equipment and instruments used for quantitative measurements are calibrated in accordance with the laboratory's formal calibration program as described in the QA manual. A summary

of the laboratory instrument/equipment calibration program is presented. Detailed calibration procedures specific to each analysis are included in method-specific SOPs which can be obtained from the laboratory.

Whenever possible, the laboratory uses recognized procedures for calibration such as those published by USEPA or ASTM. If established procedures are not available, the laboratory develops a calibration procedure based on the type of equipment, stability, characteristics of the equipment, required accuracy, and the effect of operation error on the quantities measured. Equipment requiring only periodic calibration such as balances, thermometers, and micropipettors are listed along with their respective calibration requirements in the QA manual. Whenever possible, physical reference standards associated with periodic calibrations such as weights or certified thermometers with known relationships to nationally recognized standards are used. Where national reference standards are not available, the basis for the reference standard is documented.

Other instruments that require initial and/or continuing calibration as a part of instrument usage are listed along with their respective calibration requirements in the QA manual. Initial calibrations are verified and documented for each constituent by analysis of laboratory-prepared certified independent standard solutions. Chemical reference standards used in operational calibration are obtained from recognized standards suppliers and whenever possible are traceable to NIST, A2LA, or other recognized standards.

Equipment or instruments that fail calibration or become inoperable during use are tagged to indicate they are out of calibration. Such instruments or equipment are repaired and successfully recalibrated prior to re-use.

All high resolution mass spectrometer instruments undergo extensive tuning and calibration prior to running each sample set. The calibrations and ongoing instrument performance parameters are recorded and reported as part of the analytical data package.

3.7 Acceptance Requirements for Supplies and Consumables

Supplies and consumables that may be used during field investigations include sample bottles, hoses, materials for decontamination activities, potable water, deionized water, and ASTM Type II water. Project team members obtaining supplies and consumables are responsible for assuring that the materials obtained meet the required specifications, are intact and in good condition, are available in adequate supply, and are stored appropriately until use. Project team members will direct any questions or identification of any problems regarding supplies and consumables to the Field Team Leader for resolution.

3.8 Data Acquisition Requirements (Non-direct Measurements)

This section of the QAPP describes the various sources and purpose of non-directly measured data that will be required for this investigation. The evaluation of the current site conditions requires a review of historical investigation reports that were prepared specifically for the Site.

3.9 Data Management

The objective of Data Management is to establish procedures to be used during the field investigations for documenting, tracking, and presenting investigative data. Data generated during the field investigations, as well as historical data, will be used to form the basis for conclusions and recommendations. Efficient utilization and comprehensive consideration of available data requires that the data be properly organized for review. Organization of the data shall be planned prior to actual collection to assure the generation of identifiable and usable data. This section contains procedures necessary to assure the collection of

sufficient data for accurate validation of raw data and transfer of validated data to a data management system with which it can be evaluated with minimal effort. This section also describes the operating practices to be followed by personnel during the collecting and reporting of data.

3.9.1 Purpose and Background

Data collected during the field investigations will include analytical chemistry data from biota and environmental matrices, and data on physical conditions present at the site during sample collection. These data will be integrated into an analysis of the nature and extent of COPC in environmental media and biota.

To complete this analysis, various computer programs will be utilized. The programs that are anticipated to be used are Microsoft Excel, Microsoft Access, SYSTAT, SAS, and Geographic Information Systems (GIS).

3.9.2 Data Recording

Observations made and measurements taken in the field will be recorded on appropriate project data sheets or in field logbooks. Upon completion of the field investigation, the data will be entered into a Database Management System (DBMS) and tabulated for evaluation and presentation in the field investigation report. Copies of the original data records will be attached to the report as appendices. Tissue matrix sample data will be summarized in tabular form in reports and will include sample location and other pertinent data.

All data used for meeting project objectives will be stored in an electronic database. This database will facilitate the following processes:

- Tracking COC and sample identification data;
- Reviewing and evaluating analytical data against project-specific QAPP criteria;
- Production of data tables.

An electronic data deliverable (EDD) will be submitted with the hard copy data reports. It is expected that the laboratories will perform a comparison of electronic data with the hard copy report prior to submittal to ensure that the EDD and hard copy data are identical. EDDs will be checked against the hard copy with 100% QA/QC for all detect analytes. The EDD should be submitted on a CD-ROM, with the disk label including the Laboratory Delivery Group, submittal date, laboratory name, and site description. If the EDD is resubmitted, the EDD will be labeled as "Revised".

3.9.3 Data Validation

Data validation is an integral part of the QA program and consists of reviewing and assessing the quality of data. Data validation provides assurance that the data are of acceptable quality as reported. For validity, the characteristics of importance are precision, accuracy, representativeness, comparability, and completeness. Data usability is the determination of whether or not a data set is sufficiently complete and of sufficient quality to support a decision or action, in terms of the specific DQOs. An outside firm or company specializing in data validation will independently validate analytical data generated during the project.

Analytical data will be generated by ENTRIX in EDD form, and will be submitted directly to the data validation firm for verification and validation. If necessary, exception reports will be produced. Qualified results will be loaded into the database and sent directly to ENTRIX.

The data validation process includes:

- Evaluating against laboratory and field blank criteria;
- Evaluating against accuracy criteria such as holding times, surrogates, laboratory control samples, and matrix spikes;
- Evaluating against precision criteria such as matrix spikes/matrix spike duplicates, and field and laboratory duplicates;
- Confirming that data qualifiers are assigned appropriately; and
- Uploading field sample analytical data only to the central database.

3.9.4 Data Transformation

If data transformation is performed for this study, then conversion procedures will be described in detail in the associated technical report.

3.9.5 Data Transmittal

Entering the data from field forms into the DBMS completes the integration of field data by data entry personnel. A staff scientist will review the data for completeness and accuracy by comparing the values to the original field data.

Analytical laboratory data are provided in both a hard copy and in EDD format. The electronic data are provided in a specified format that will be uploaded to intermediate files, reviewed for completeness and accuracy by the Project Liaison before uploading to the project DBMS.

3.9.6 Data Analysis

Data analysis (e.g. computation of summary statistics, standard errors, confidence intervals, etc.) will be conducted for this project.

3.9.7 Data Tracking

The Project Manager is ultimately responsible for all activities conducted during site activities, including data management. The Project Manager has the authority to enforce proper procedures as outlined in this plan and to implement corrective procedures to assure the accurate and timely flow and transfer of data. The Project Manager will review the final data reports.

Data will be generated from the field surveys and environmental sampling and analysis. The generators of data will be responsible for accurate and complete documentation of data required under the task, and for assuring that these data are presented to their supervisor in a timely manner.

The FTL will be responsible for the day-to-day monitoring of data collected in the field. He/she assures that data are collected in the format specified in this QAPP and route data to ENTRIX to be placed in the project files at the end of field collection activities. Original documents will be maintained in the ENTRIX central project file.

The FTL shall also be responsible for evaluating biological and field collected data. He/she reviews biological data for accuracy and completeness. The project manager for each component of the study will assure that representations of current site conditions are accurate and complete.

The Project Liaison will be responsible for the day-to-day monitoring of activities related to the generation and reporting of chemical data. He/she ensures that samples are analyzed according to the

specified procedures; that data are validated; and that the data are properly coded, checked for accuracy (QA), and entered into the data management system. He/she assures the data are then routed to ENTRIX to be placed in the project files.

3.9.8 Data Storage and Retrieval

A project file will be established for the storage of original data, historical data, written documents, and data collected or generated during the field investigation. The format for the file will follow the central filing system procedure list, which consists of the following categories:

- Correspondence;
- Budgets;
- Contracts;
- Field Data
    - general field data
    - field notes
    - raw data
- Figures and Maps;
- Permits;
- Paper and electronic copies of field collected data – both paper and PDA data
- Laboratory Data and QA/QC Documents;
- Chains of Custody;
- Photographs;
- Reports;
- Schedules;
- Background.

All materials will be dated, carry the initials of the person responsible for the preparation of the document, and bear the project number. The file copies will include peer review sign-off on the calculation sheets and editing review sheets where applicable.

Access to the project files will be limited to those personnel assigned to this project. The Project Manager maintains overall responsibility for the project files and assures that appropriate documents are filed. All documents relating to the project shall be controlled to assure proper distribution, filing, and retrieval. The document control shall also assure that revisions are properly recorded, distributed, and filed. ENTRIX staff maintain the project files.

ENTRIX staff will handle all documents submitted to the project file and will assure that the documents are appropriately filed by category and placed in the correct project file. Once filed, documents are available to ENTRIX staff and may be removed from file for use by signing out the material.

4.0 ASSESSMENT AND OVERSIGHT

This section presents the internal and external checks (assessments) that have been built into this project to assure that:

- Elements of this QAPP have been correctly implemented as prescribed for all investigations conducted;
- The quality of the data generated is adequate and satisfies the DQOs that have been identified in this QAPP; and
- Corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

Assessment activities may include surveillance, inspection, peer review, management systems review, readiness review, technical systems audit, performance evaluation, and data quality assessment.

4.1 Assessment Activities

The following subsections identify the planned assessment and oversight activities to assure the objectives identified above are attained for field and laboratory operations. The QA Manager and/or the Project Manager may also identify additional assessment activities to be performed during the course of the project based upon findings of the planned assessment activities described below.

4.1.1 Assessment of Field Operations

The QA Manager and/or other designated members of the project team will conduct internal assessments of field operations, where appropriate. The assessment activities will evaluate field operations performance issues such as:

- Are sampling operations being conducted in accordance with the QAPP?;
- Are the sample labels being filled out completely and accurately?;
- Are the COC records complete and accurate?;
- Are the field notebooks being filled out completely and accurately?; and
- Are the sampling activities being conducted in accordance with SOPs?

Planned assessment activities to evaluate these and other field operations performance issues include surveillance (frequent review) of sample collection documentation, sample handling records (COC forms), field notebooks, and field measurements, and the performance of unannounced field operations audits.

The team member conducting the assessment activity will report the results of any assessment activities to the Project Manager. Assessment activity reports will include the findings and identification of any corrective actions taken or planned.

4.1.2 Assessment of Laboratory Operations

Michigan State University Aquatic Toxicology Laboratory and AgriQuality have performed congener-specific PCDD/F and PCB analysis for various clients and agencies in a variety of environmental matrices. The data generated for those projects have been approved. CRMs are analyzed routinely and

the measured values are within ±20% of the actual concentrations. The laboratories also have ongoing internal audit programs implemented to monitor the degree of adherence to their policies, procedures, and standards. The internal audit program is described in the QA manual and includes systems audits, performance evaluations, data audits, and spot assessments. Laboratory personnel who are independent of the area(s) being evaluated will conduct internal audits. The laboratory also participates in external audits conducted by regulatory agencies and other clients. Project-specific assessments of laboratory operations are described below.

The Project Liaison will be in contact with the Project Manager on a weekly basis while samples collected during this investigation are being analyzed. This will allow assessment of progress in meeting DQO and the identification of any problems requiring corrective actions early in the investigative process. The Project Liaison will promptly report problems identified, corrective actions taken, and recommendations as appropriate for additional corrective action to the Project Manager. The Project Manager will review the problem and provide for the swift implementation of any outstanding corrective actions. In addition, contact between the Project QA Manager and the Independent Data Auditor (see Sections 5.1 and 5.3) could result in the need for a laboratory audit. The Project QA Manager will report the audit findings and any recommendations for corrective action to the Project Manager, the Project Liaison, and the laboratory. The Project Liaison will be responsible for working directly with the laboratory to assure the prompt resolution of any problems identified.

4.2 Reports to Management

This subsection discusses reports internal to the project team. External reports are discussed in Section 2.7.2.

Reports to management include project status reports, the results of surveillance evaluations, field and/or laboratory audits, and data quality assessments. These reports will be directed to the Project Manager who has ultimate responsibility for assuring that any corrective action response is completed, verified, and documented.

Final reports produced during this investigation will include a quality assurance section with the following information:

- Identification of problems that required corrective action and resolution of the problems;
- Data quality assessment in terms of precision and accuracy and how they affect the usability of the analytical results;
- Limitations of any qualified results and a discussion of any rejected results; and
- Discussion of the field and laboratory QA/QC sample results.

All written communications between project team members including reports to project management will be maintained in the project files.

5.0 DATA VALIDATION AND USABILITY

This section of the QAPP provides a description of the QA activities that will occur after the data collection phase of the project is completed. Implementation of this section will determine whether or not the data conform to the specified criteria, thus satisfying the project objectives.

5.1 Data Review, Validation, and Verification

Data validation is the process of reviewing data and accepting, qualifying, or rejecting data on the basis of sound criteria using established EPA guidelines. The laboratory will report laboratory data generated during field investigations as Level IV data packages. All of these data will be subjected to full data validation conducted by an independent data validator as discussed below in Section 5.1.1.

5.1.1 Independent Data Validation Protocols

While the actual procedures used will be determined by the validator the validation approach will consist of a systematic review of the analytical results, associated QC methods and results, and all of the supporting data. Specific data package review procedures can be found in SOP #802 "Data Package Review" included in this Work Plan. Best professional judgment in any area not specifically addressed by EPA guidelines will be utilized as necessary and described in the Usability Assessment portion of the data validation report.

Data will be validated according to applicable guidelines set forth in the following sources and guidelines to ensure compliance with the Federal Information Quality Act:

- "Data Package Review" SOP #802 Aquatic Toxicology Laboratory, National Food Safety and Toxicology Center, Michigan State University, E. Lansing, MI 48824-1222 USA
- "Guidance for Data Usability in Risk Assessment (Part A)," U.S. EPA Publication 9285.7-09A, U.S. EPA, April, 1992.
- "Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by the Environmental Protection Agency" U.S. EPA Publication EPA/260R-02-008, October, 2002.
- "Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by Federal Agencies." Federal Register, 67, No. 36, pp8451-8460, February 22, 2002.

Data validations will include a data completeness check of each data package, a transcription check for sample results, and a thorough review of all laboratory reporting forms and the associated raw data for QA/QC issues. Specifically, this review will include:

- Review of data package completeness;
- Review of the required reporting summary forms and all associated raw data to determine if the QC requirements were met and to determine the effect of exceeded QC requirements on the precision, accuracy, and sensitivity of the data;
- Review of the overall data package to determine if contractual requirements were met (based upon National Functional Guidelines);

- Review of raw data and all calculations associated between one and a minimum of 10% of all samples to determine if the sample results and quantitation limits were correctly calculated and reported;
- Review of additional QA/QC parameters, such as field blank contamination, to determine technical usability of the data; and
- Application of standard data quality qualifiers to the data.

In addition, each data validation will include a comprehensive review of the following QA/QC parameters as indicated in the National Functional Guidelines:

- Holding times (to assess potential for degradation that will affect accuracy)
- GC/MS instrument check (to assess accuracy and sensitivity of method)
- Initial calibration (to assess method sensitivity)
- Continuing calibration (to assess method sensitivity)
- Blanks (to assess contamination for all compounds)
- System monitoring compounds (to assess method accuracy)
- MS/MSD or laboratory fortified blanks (to assess accuracy of the methods and precision of the method relative to the specific sample matrix)
- Internal standards (to assess method accuracy and sensitivity)
- Target compound identification
- Compound RL and MDL (to assess sensitivity as compared to project-specific requirements)
- System performance (to assess accuracy and precision)

5.1.2 ENTRIX Internal Data Quality Control Procedures

ENTRIX has established an internal QA Program to assure that all project analytical data are tracked within a COC database system and are of reliable and comparable data quality. The Project QA Manager will be responsible for assuring that ENTRIX internal QC procedures are followed for all project analytical data.

The COC database system allows ENTRIX to track samples and their analytical results to ensure that the project data quality objective for completeness is met. Samples and analytical data are tracked in a COC database system by their COC number. The COC number along with the date the laboratory received the samples for analyses are entered into the COC database system from the information on the field copy of the COC. When the final laboratory reports are completed, the laboratory report number along with the date and initials of the ENTRIX personnel who have reviewed the report is entered into the COC database system according to the COC number.

A limited internal data validation is performed on all project analytical data when the final report is reviewed by ENTRIX. The limited data validation will include a data completeness review of each data package, and a limited review of QA/QC parameters as indicated in the National Functional Guidelines to assure that all project analytical data are of reliable and comparable data quality. Specifically, the following QA/QC parameters will be reviewed:

- Holding times (to assess potential for degradation that will affect accuracy);
- Blanks (to assess contamination for all compounds);
- MS/MSD or Laboratory Control Spike/Spike Duplicates (to assess accuracy of the methods and precision of the method relative to the specific sample matrix);
- Internal Standards (to assess method accuracy and sensitivity);
- Compound RL and MDL (to assess sensitivity as compared to project-specific requirements); and
- Field Duplicate RPDs (to assess precision of the method relative to field sampling techniques, the specific sample matrix, and representativeness of the sample aliquot to the area sampled).

The results of this limited data validation and any corrective actions implemented are recorded on a QA/QC worksheet. The data reviewer will initial and date the QA/QC worksheet. The Project Manager will provide secondary review of the QA/QC worksheet and will also initial and date the QA/QC worksheet. The initialed and dated QA/QC worksheet will be attached to the final analytical laboratory report that is retained in the project files.

5.2 Validation and Verification Methods

The data validation process is conducted to assess the effect of the overall sampling and analysis process on the usability of the data. There are two areas of review: laboratory performance evaluation and the effect of matrix interferences. Evaluation of laboratory performance is a check for compliance with the method requirements and is a straightforward examination. The laboratory either did or did not analyze the samples within the QC limits of the analytical method and according to protocol requirements. The assessment of potential matrix effects consists of a QC evaluation of the analytical results and also the results of testing blank, duplicate, and matrix spike samples, and then assessing how, if at all, the matrix effect will impact the usability of the data.

All analytical data will be supported by a data package. The data package contains the supporting QC data for the associated field samples. The data validation report deliverables will include the following information:

- A comprehensive narrative detailing all QC exceedances, explaining qualifications of data results. In cases where data are qualified due to quantifiable QC exceedances, the bias (high or low) will be identified;
- Data summary tables in Microsoft Access format reporting all data results with the qualifiers that were added during the data validation review. These tables will include sample ID, laboratory ID, date sampled, sample type (e.g., field duplicate, field blank), units, concentration of analytes, and validation qualifiers. These tables may be modified to report other information as needed (such as depth of soil samples, date analyzed, dilution factor);
- Re-submittal requests sent to the laboratory indicating missing information, verification of analytical information, etc.; and
- Electronic data deliverables will be compatible with the project database. These electronic deliverables will contain the validated results and qualifications as presented in the data summary tables of the validation reports. Additionally, the validation reports can be submitted in electronic format for inclusion in interim RI data deliverables.

Before the laboratory releases each data package, the laboratory must carefully review the sample and laboratory performance QC data to verify sample identity and also the completeness and accuracy of the sample and QC data. This is performed through three levels of laboratory data review starting with 100% verification performed by the laboratory analyst, followed by a second-level review performed by a peer, supervisor, or designee. The laboratory Project Manager performs the third and final laboratory review to assure that project requirements are met for the analyses performed.

Data validation is at times based on best professional judgment. In order to achieve consistent data validation, data worksheets will be completed for each data validation effort. A data review worksheet is a summary form on which the data validator records data validation notes and conclusions specific to each analytical method. The worksheets will help the validator to track and summarize the overall quality of the data. Sample results will then be qualified as appropriate, following EPA protocols. Samples that do not meet the acceptance limit criteria will be indicated with a qualifying flag, which is a one or two-letter abbreviation that indicates a problem with the data (Table 5-1).

The data verification process begins once the data packages for each project have been validated. During verification, the entire data set will be verified for overall trends in data quality and usability. Information summarized as part of the data quality verification will include frequencies of detection, dilution factors that might affect data usability, and patterns of target compound distribution. The data set also will be evaluated to identify potential data limitations or uncertainties in the laboratory. The trend analysis results will be included in the validation summary report, which will be submitted to the Project Manager at the end of the field effort. The validation report and notes will be archived with the analytical data.

5.3 Reconciliation with User Requirements

The Independent Data Auditor will provide an assessment of the usability of the validated data compared to the data validation criteria and DQOs. The usability assessment will be performed based on Guidance for Data Usability in Risk Assessment (EPA 1992) and best professional judgment. The Independent Data Auditor will delineate major and minor deficiencies in the data, their effects on the reported results, and determination of usability for each compound reported in each sample included in the data package. The usability assessment will provide an overall summary of data quality. It defines acceptability or problems with accuracy, precision, sensitivity, and representativeness of the results with clear guidance to the data users of the uncertainties in the data that have been qualified as estimated (J) and a quantification of these uncertainties (e.g., bias high by a maximum of 80%), wherever possible. The Independent Data Auditor may determine specific results to be unusable because of cumulative effects of QC exceedances. Alternatively, based upon the EPA guidelines and best professional judgment, the Independent Data Auditor may determine specific results to be usable for DQOs when they are not significantly outside the QC criteria.

The final activity of the data validation process is to assess whether the data meets the DQOs. The final results, as adjusted for the findings of any data validation/data evaluation, will be checked against the DQOs and an assessment will be made as to whether the data are of sufficient quality to support the DQOs. The decision as to data sufficiency may be affected by the overall precision, accuracy, and completeness of the data as demonstrated by the data validation process. If the data are sufficient to achieve project objectives, the project manager will release the data and work can proceed. If the data are insufficient, corrective action will be required.

Table 5-1. Data Validation Qualifiers.

Qualifier	Explanation of Qualifier
Organic Analyses	
U	The compound was analyzed for, but was not detected above the reported method detection limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
UJ	The analyte was not detected above the reported method detection limit. However, the reported limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
Inorganic Analyses	
U	The compound was analyzed for, but was not detected above the reported method detection limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
UJ	The analyte was not detected above the reported method detection limit. However, the reported limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
B	The analyte was positively identified; the reported concentration is greater than the instrument detection limit, but less than the QAPP specified Reporting Limit.

6.0 REFERENCES

ASTM D 2216-90. Moisture Analysis of Soils.

ASTM D 422-63. Standard Test Method for Particle-Size Analysis of Soils.

ChemRisk Division McLaren Hart Environmental Engineering Corporation, Alameda, CA, 1996. Off-Site Biological Inventory and Evaluation Report. Prepared for PPG Industries, Inc. Lake Charles, LA.

Duke, James H., 1985. Calcasieu River Basin, Louisiana Modeling Study. Prepared for Department of Environmental Quality, State of Louisiana.

ENTRIX (2004). Final Report: Concentrations of Dioxins, Furans, and 2,3,7,8-TCDD equivalents in wild game samples taken from the Tittabawassee River floodplain. (IN PREPARATION).

Giesy, J.P., Ludwig, J.P., and Tillitt, D.E. (1994): Deformities in birds of the Great Lakes region. Assigning causality. *Environ. Sci. Technol.* 28, 128A-135A.

Gilberston, M., Kubiak, T.J., Ludwig, J.P., Fox, G.A. 1991. Great Lakes Embryo Mortality, Edema, and Deformities Syndrome (GLEMEDS) in colonial fish-eating birds: Similarity to chick-edema disease. J. Toxicol. Environ. Health 33: 455-520.Hilsherova, K., Kannan, K., Nakata, H., Yamashita, N., Bradley, P., McCabe, J., Taylor, A.B., Giesy, J. P., 2003. Polychlorinated Dibenzo-p-dioxin and Dibenzofuran Concentration Profiles in Sediments and Flood-Plain Soils of the Tittabawassee River, Michigan. *Environ. Sci. Technol.* 37, 468-474.

Long, E.R., D.D. MacDonald, S.L. Smith and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Mgmt.* 19:81-97.

Ludwig, J.P., Kurita-Matsoba, H., Auman, H.J., Ludwig, M.E., Summer, C.L., Giesy, J.P., Tillitt, D.E., Jones, P.D. 1996. Deformities, PCBs and TCDD-equivalents in Double-Crested cormorants (*Phalacrocorax auritus*) and Caspian Terns (*Hydroprogne caspia*) of the Upper Great Lakes 1986-1991: Testing a cause-effect hypothesis. *J. Great Lakes Res.* 22: 172-197.

MDEQ. 2002. Baseline Chemical Characterization of Saginaw Bay Watershed Sediments – A report to the Office of the Great Lakes, Michigan Department of Environmental Quality.

MDEQ. 2003a. Phase II Tittabawassee/Saginaw River Dioxin Floodplain Sampling Study June 2003. Michigan Department of Environmental Quality Remediation and Redevelopment Division.

Murray, F.J., Smith, F.A., Nitchke, K.D., Humiston, C.G., Kociba, R.J., Schwetz, B.A. 1979. Three generation reproduction study of rats given 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the diet. *Toxicol. Applied Pharmacol.* 50: 241-252.

Office of Management and Budget (2002). Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by Federal Agencies." Federal Register, 67, No. 36, pp8451-8460, February 22, 2002.

Okey, A.B., Riddick, D.S., and Harper, P.A. 1994. The Ah receptor: mediator of the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related components. *Tox. Lett.* 1: 1-22.

Powell, D.C., Aulerich, R.J., Meadows, J.C., Tillitt, D.E., Powell, J.F., Restrum, J.C., Stromberg, K.L., Giesy, J.P., and Bursian, S.J. 1997. Effects of 3,3',4'4,',5-pentachlorobiphenyl (PCB 126), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), or an extract derived from field collected cormorant eggs injected into Double-Crested cormorant (*Phalacrocorax auritis*) eggs. *Environ. Toxicol. Chem.* 16: 1450-1455.

Research Triangle Institute, 1990. Toxics Study of the Lower Calcasieu River. Prepared for Water Quality Management Branch, EPA Region 6, Dallas, TX.

Tillitt, DE, Gale, RW, Meadows, JC, Zajicek, JL, Peterman, PH, Heaton, SN, Jones, PD, Bursian, SJ, Kubiak, TJ, Giesy, JP, Aulerich, RJ. 1996. Dietary exposure of mink to carp from Saginaw Bay. 3: Characterization of dietary exposure to planar halogenated hydrocarbons, dioxin equivalents, and biomagnification. *Environ Sci Technol* 30:283-291.

U.S. EPA (United States Environmental Protection Agency). 1992. Guidance for Data Usability in Risk Assessment (Part A), U.S. EPA Publication 9285.7-09A, U.S. EPA, April 1992.

U.S. EPA (United States Environmental Protection Agency). 1993. Contract Laboratory Program, Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, Document Number ILMO3.0; "Methods for Determination of Inorganic Substances in Environmental Samples," EPA/600/R-93/100.

U.S. EPA (United States Environmental Protection Agency). 1994a. EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations. Draft Interim Final. EPA QA/R-5. Quality Assurance Division. United States Environmental Protection Agency, Washington, DC.

U.S. EPA (United States Environmental Protection Agency). 1994b. Guidance for the Data Quality Objectives Process. External Working Draft. EPA QA/G-4. Quality Assurance Division. United States Environmental Protection Agency, Washington, DC.

U.S. EPA (United States Environmental Protection Agency). 1994c. Test Methods for Evaluating Solid Waste. Final Update IIA. Physical/Chemical Methods. SW-846. Office of Solid Waste and Emergency Response, Washington, DC. 1994.

U.S. EPA (United States Environmental Protection Agency). 1994d. Contract Laboratory Program, Statement of Work for Organic Analysis, Document Number OLMO3.1.

U.S. EPA (United States Environmental Protection Agency). 1994e. National Functional Guidelines for Organic Data Review Multi-Media, Multi-Concentration, ILMO 1.0 and Low Concentration Water, OLCO 1.0, EPA/540/R-94/090, ("National Functional Guidelines").

U.S. EPA (United States Environmental Protection Agency). 1998. Guidance for Quality Assurance Project Plans, EPA QA/G-5. Office of Research & Development. EPA/600/R-98/018. Quality Assurance Division. United States Environmental Protection Agency.

U.S EPA (United States Environmental Protection Agency). 2002. Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by the Environmental Protection Agency" U.S. EPA Publication EPA/260R-02-008, October, 2002.

Van den Berg, M., L. S. Birnbaum, A. T. C. Bosveld, B. Brunstrom, P. M. Cook, M. Feeley, J. P. Giesy, A. Hanberg, R. Hasegawa, S. Kennedy, T. J. Kubiak, J. C. Larsen, F. X. R. van Leeuwen, A. K. D. Liem, C. Nolt, R. E. Peter, L. Poellinger, S. Safe, D. Schrenk, D. E. Tillitt, M. Tysklind, M. Younes, F. Waern, and T. Zacharewski. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* 106:775-792, 1998.

6.1 Associated Standard Operating Procedures

SOP #	Title
TR203	Homogenization of Tissue Samples
TR210	Extraction and Analysis of PCBs and Non-ortho Coplanar PCBs in Biological and Environmental Matrices
TR211	Mono-and Non-*ortho PCB* Analysis by GC-MSD using Chrompack CP SIL 5/C18
TR212	Glassware Cleaning: General and Trace Organic Analysis
TR213	Extraction and Analysis of 2,3,7,8 Substituted Polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofurans (PCDF) in Sediment & Biota Samples Using the High Resolution Gas Chromatography High Resolution Mass Spectrometry
TR214	Documentation, Preservation, handling, and Tracking of Samples for Analysis
TR401	Sample Management: Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal
TR402	Maintenance of Sample Integrity, and Proper Usage of Refrigerators, Freezers, and Liquid Nitrogen Dewars
TR802	Data Package Review