United States
Environmental Protection
Agency

Office of Toxic Substances
Exposure Evaluation Division
Washington, DC 20460

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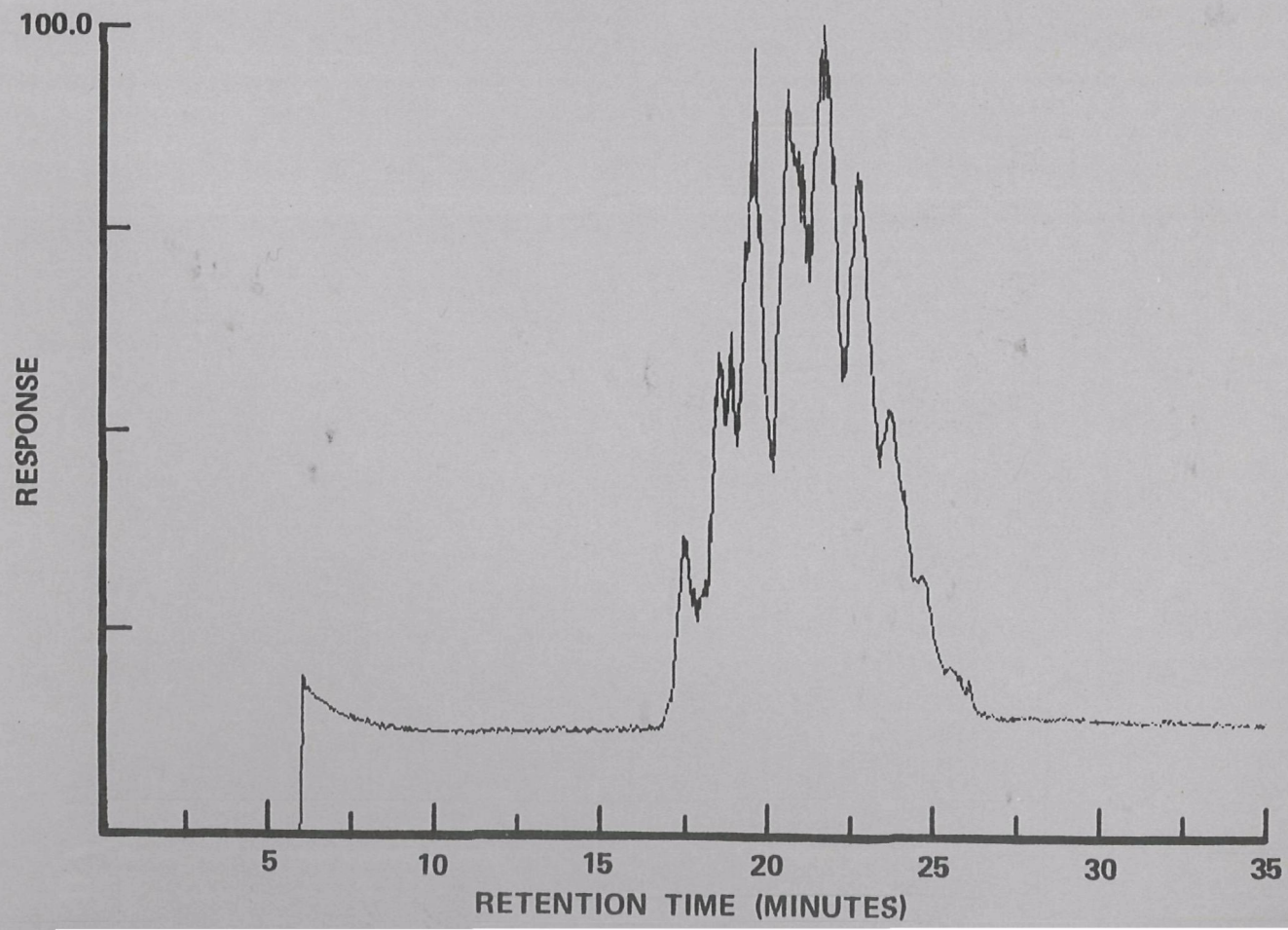
Toxic Substances

EPA

# Chlorinated Paraffins

## A Report on the Findings from Two Field Studies Sugar Creek, Ohio Tinkers Creek, Ohio

## Volume II – Appendix D, The Quality Assurance Project Plan



SECTION 1.0

# CHLOROPARAFFIN ENVIRONMENTAL FIELD STUDY

## QUALITY ASSURANCE PROJECT PLAN

EPA/MRI CONTRACT NO. 68-02-4252
WORK ASSIGNMENT NO. 53

EPA/BATTELLE CONTRACT NO. 68-02-4243

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SECTION 2.0

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# SECTION 3.0

# PROJECT DESCRIPTION

The Environmental Protection Agency/Office of Toxic Substances (EPA/OTS) under the Existing Chemicals Program has initiated simple field studies to screen selected waterbodies for the presence of chlorinated paraffins (CPs). The information gained from these field studies will be coupled with other environmental and health studies and collectively contribute to a risk assessment for this chemical.

Studies conducted by both the U.S and Europe have found CPs in environmental samples including sediment, tissue, water and soil. However, the validity of the analytical methods used to quantify these samples has been debated fostering a continuing effort to solve significant analytical and interference problems. Therefore, a critical first step to the development of the field studies discussed in this Project Plan was to develop and validate an analytical method capable of measuring these constituents in different environmental matrices. A complete description of this effort and the analytical method of choice is provided in Appendix C.

The objective of this field study effort is to collect information that will help EPA determine, preliminarily, if chlorinated paraffins exist in the water environment, i.e. the water column (including suspended material), the sediment and in biological tissue, and at what environmental levels. Because chlorinated paraffins are used predominantly in the lube oil business, this study is designed based on the assumption that if CPs exist in the aquatic environment they will most likely be found in waters receiving discharge from CP manufacturers, processors of lubricating oils, and users of these oils. Therefore, for the purposes of this study, two areas have been selected for study and will, therefore, represent the water environment as expressed in the statement of objective. The first is Sugar Creek in Dover Ohio; the second is Tinkers Creek in Bedford, Ohio. Chlorinated paraffins will be identified by chain length categories and will be quantified in four environmental matrices.

## 3.1 Scope of Work

The scope of work will consist of the following subtasks:

1. Develop and field validate the analytical method for determining CPs of differing chain lengths for water column, suspended solids, sediment and tissue.

2. Develop a QA/QC project plan and a field study and sampling design for the sites selected for the study. Combine these to form one document.

3. Conduct a preliminary site visit (reconnaissance survey) of the study sites.

4. Finalize the study and sampling design with information obtained from the preliminary site visit.

5. Collect field samples at the sites selected for the study following the protocol expressed in this QAPP.

6. Perform the necessary laboratory analysis of the samples collected in the field.

7. Analyze data; prepare results and conclusions.

8. Write and submit draft and final reports.

Subtasks 2, 3, 4, 7 and 8 will be developed cooperatively by Exposure Evaluation Division's Field Studies Branch and Design and Development Branch and their respective contractors, Midwest Research Institute and Battelle Columbus Division. Subtask 5 will be completed by Midwest Research Institute and its subcontractor, PEI Associates. Subtasks 1 and 6 will be completed by MRI. The experimental design of the field study will be developed by the Design and Development Branch and its contractor, Battelle Columbus Division.

# SECTION 4.0

# PROJECT ORGANIZATION AND MANAGEMENT

This project is being conducted as part of OTS' Existing Chemicals Program. Focus and direction for the study is provided by a Technical Team of OTS experts. The field study will be conducted largely by the Midwest Research Institute and its contractor PEI Associates under contract to the Field Studies Branch. The experimental design, data analyses and results and conclusions for the study will be developed by the Design and Development Branch and its contractor, Battelle.

The overall project organization chart is shown in Figure 4.1.

## 4.1 Midwest Research Institute:

The MRI project organizational chart is shown in Figure 4.2.

### 4.1.1 Project Management

Mr. Paul Constant will represent management and serve as program manager. He will be assisted in this effort by Mr. John Hosenfeld. Together they will:

- Assure that all necessary resources are available.
- Assure that the Quality Assurance Manager (QAM)/Quality Assurance Coordinator (QAC) is fully informed and involved in the project.
- Assure that all personnel are informed of project QA policy.
- Review all communication from the QAM/QAC regarding the project.
- Assure that any problems, deviations, etc. reported by the QAM/QAC receive immediate corrective action.

### 4.1.2 Quality Assurance Manager/Quality Assurance Coordinator

Ms. Carol Green, Quality Assurance Manager, will represent QA management. She will be assisted by Mr. Jack Balsinger who will serve as QAC. Together they will:

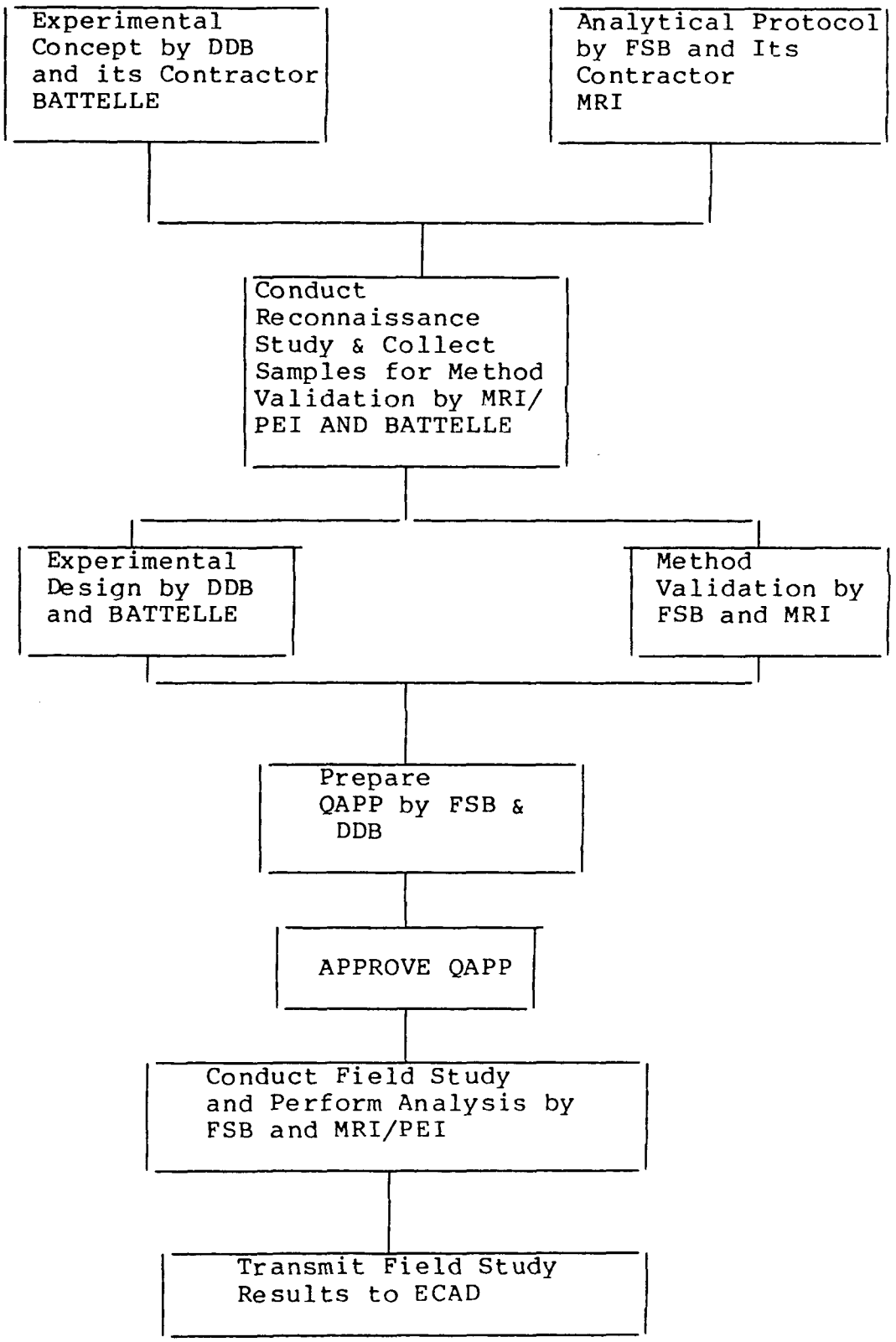


FIGURE 4-1 - Overall Project Organization

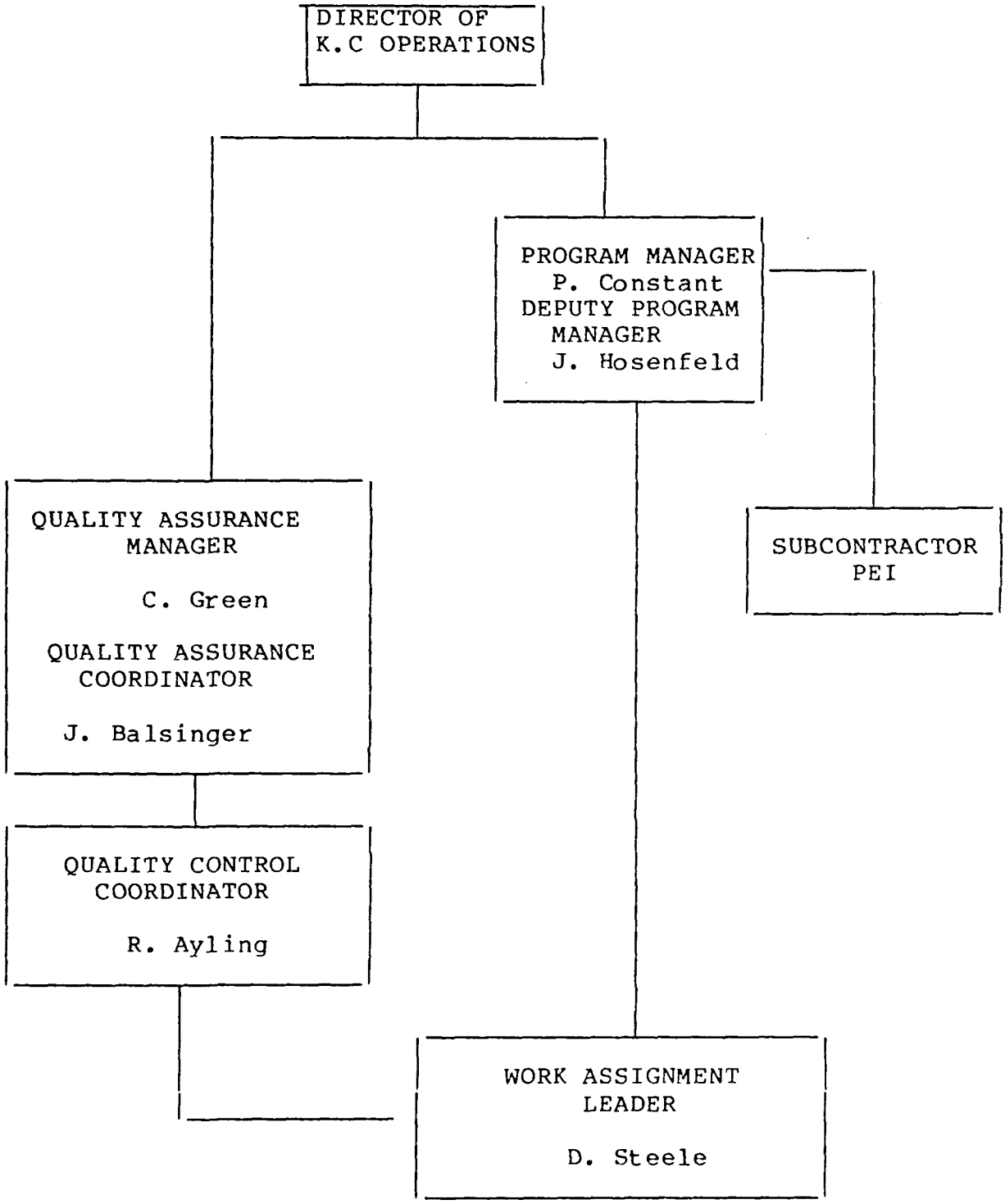


Figure 4-2 MRI Project Organizational Chart

- Assure that all QA policies and procedures are available and understood by project staff by conducting training courses.

- Assure MRI Management that the facilities, equipment, personnel, methods, records and controls are consistent with project objectives/requirements by conducting or directing inspections and/or audits. These inspection/ audit results are reported to project and MRI Management. Corrective action is requested in these reports.

- Help prepare the project QA plan.

- Reinspect or audit to assure that appropriate corrective actions were implemented. Report unresolved corrective actions to MRI's Associate Director of K.C. Operations and the Senior Vice President for resolution.

- Review and audit data reports and supporting evidence prior to submission to EPA.

- Prepare and direct the preparation of QA reports to be submitted to EPA.

4.1.3 QC Coordinator

Mr. Randy Ayling will serve as QCC. He will:

- Conduct systems audit(s) and report findings to the QAM/QAC.

- Prepare performance audit samples.

- Review notebooks, chromatograms, printouts, and other hard copy information during systems audits.

- Report audit findings to project leader and program management after QAM/QAC approval.

4.1.4 Work Assignment Leader

Mr. David Steele will be the work assignment leader. He will:

- Help prepare the project QA plan.

- Be responsible for training staff where required.

- Be responsible for sample receipt and traceability.

- Enforce instrument calibration and maintenance procedures.
- Maintain document control of lab and sampling data, notebooks, records, and other hard copy information.
- Review and approve all data prior to submittal to EPA.
- Review/validate raw data (e.g., notebooks, forms, strip charts, etc.).
- Ensure that any deviations from protocol are approved and documented.
- Be responsible for analytical data traceability.
- Take correction action on any problems and communicate them in writing to the QAC/QAM, the QCC, and the program and department managements.
- Prepare and submit monthly and triannual reports.
- Prepare and submit other reports as requested by the work assignment manager in conjunction with project staff.

## 4.2 PEI Associates

The PEI project organizational chart is shown in Figure 4-3.

### 4.2.1 Project Management

Mr. Les Ungers will represent management and serve as Program Manager. Mr. Unger's responsibilities are:

- Assure that all necessary resources are available.
- Assure that the Quality Assurance Manager(QAM)/ Qualty Assurance Coordinator (QAC) is fully informed and involved in the project.
- Assure that all personnel are informed of project QA policy.
- Review all communication from the QAM/QAC regarding the project.
- Assure that any problems, deviations, etc. reported by the QAM/QAC receive immediate corrective action.

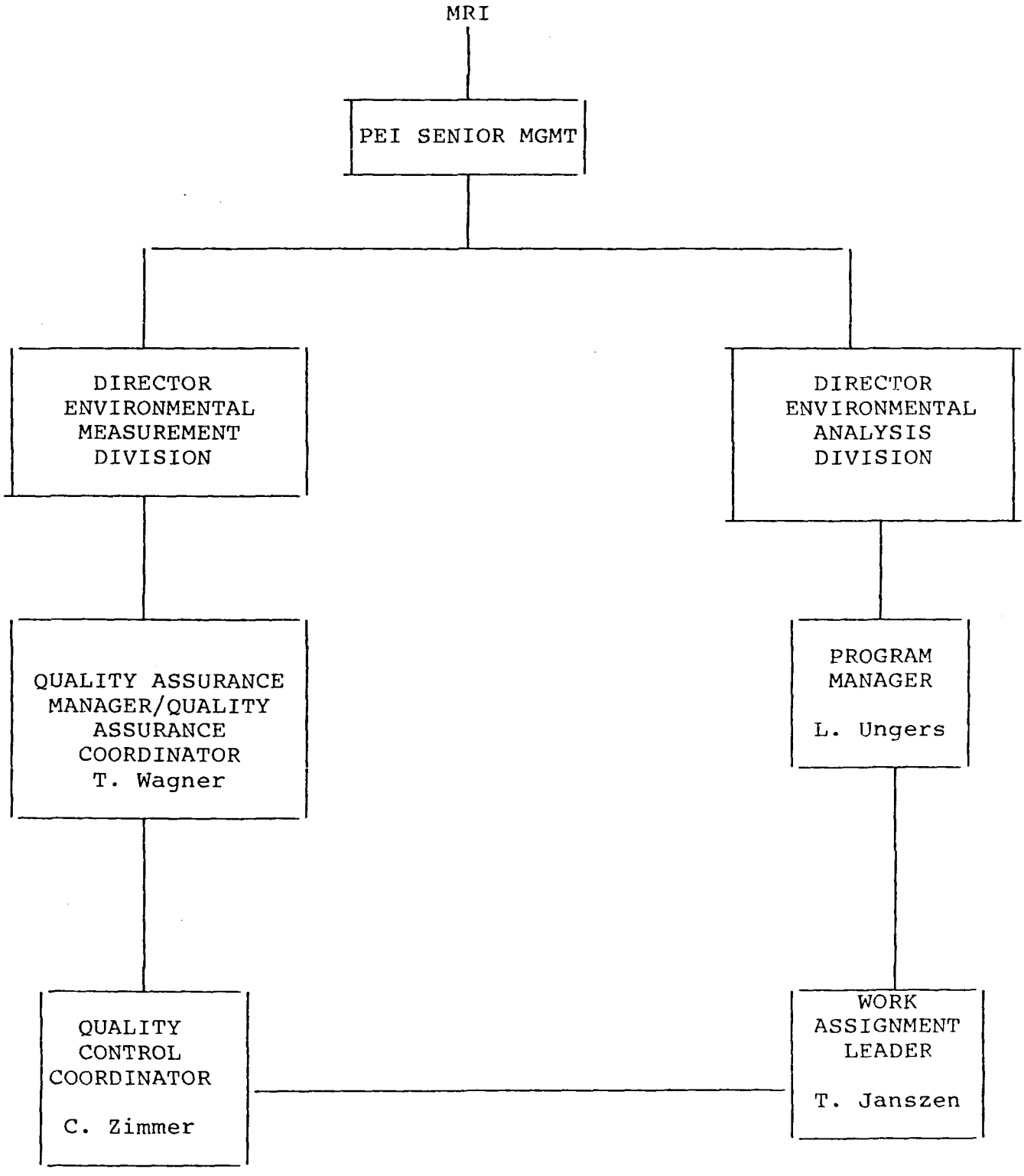


FIGURE 4.3 - PEI ORGANIZATIONAL CHART

4.2.2 Quality Assurance Manager/ Quality Assurance Coordinator

Mr. Thomas Wagner, Quality Assurance Manager, will represent QA management. Mr. Wagner's responsibilities are:

- o Assure that all QA policies and procedures are available and understood by project staff by conducting training courses.
- o Assure PEI Management that the facilities, equipment, personnel, methods, records and controls are consistent with project objectives/requirements by conducting or directing field sampling efforts.
- o Help prepare the QA project plan.
- o When necessary, assure that appropriate corrective actions were implemented. Report unresolved corrective actions to PEI's Program Manager.
- o Review reports and supporting evidence prior to submission to MRI.
- o Prepare and direct the preparation of QA reports to be submitted to MRI.

4.2.3. QC Coordinator

Mr. Charles Zimmer will serve as QCC. He will:

- o Review notebooks, and other hard copy information during the performance of the work assignment.
- o Report findings to the Project Leader and program Management after QAM/QAC approval.

4.2.4 Work Assignment Leader

Mr. Thomas Janszen will be the work assignment leader. He will:

- o Help prepare the QA project plan.
- o Be responsible for training staff, where required.
- o Be responsible for sample collection and transport of these samples to MRI.
- o Maintain document control of sample collection, notebooks, records, and other hard copy information.

- Review and approve all data prior to submittal to MRI.
- Review/validate raw data (e.g., notebooks, forms, strip charts, etc.)
- Ensure that any deviations from protocol are approved and documented.
- Take corrective action on any problems and communicate them in writing to the QAM/QAC, the QCC and the Program and Department Management.
- Prepare and submit monthly and triannual reports.
- Prepare and submit other reports as requested by the Work Assignment Manager in conjunction with Project staff.

## 4.3 Battelle Columbus Division

The Battelle Columbus Division project organizational chart is shown in Figure 4-4.

### 4.3.1 Project Management

Dr. Jean Chesson will represent management and serve as program manager.

### 4.3.2 Quality Assurance Administrator

Ms. R. Mayer will represent QA management.

### 4.3.3 Work Assignment Leader

Dr. J. Chesson is the work assignment leader. She will be assisted by Mr. Robert Heath, Consultant to Battelle. Responsibilities include:

- Help prepare the QA plan.
- Prepare the experimental designs.
- Participate in the reconnaissance survey.
- Contribute to the field activities.
- Review/validate data collected in the field; formulate results.
- Analyze data.
- Contribute data analyses, results and conclusions to the final report.

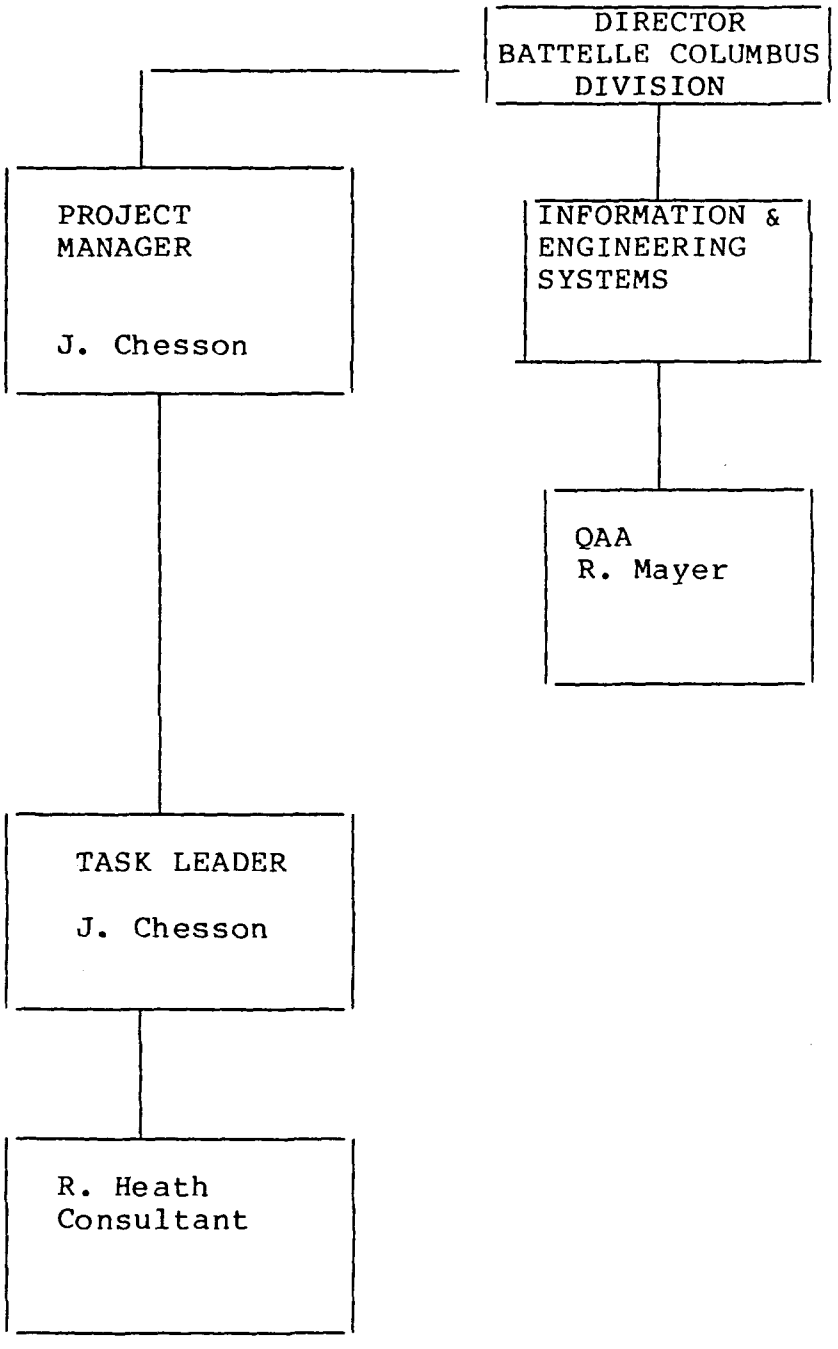


Figure 4-4 Battelle Columbus Division Project Organizational Chart

# SECTION 5

## PERSONNEL QUALIFICATIONS

### 5.1 Midwest Research Institute

Mr. Paul C. Constant, and Mr. John Hosenfeld will serve as program manager and deputy manager, respectively. Mr. Hosenfeld will assist Mr. Constant. Their credentials were previously submitted in the proposal for this contract. Mr. David Steele will serve as the Work Assignment Leader. Mr. Steele has served as Work Assignment Leader on Tasks 39 and 42 during the previous contract and is Work Assignment Leader on Task 53 of the present contract. His credentials were submitted in the proposal for this contract.

Ms. Carol Green will be the Quality Assurance Manager. She has served in this capacity since May 1983. Her credentials were previously submitted in the proposal for this contract.

Mr. Jack Balsinger will be the Quality Assurance Coordinator. He has been assigned to the QA Unit since June 1985. His credentials were previously submitted in the proposal for this contract.

Mr. Randy Ayling will serve as Quality Control Coordinator. He is skilled in extraction techniques and mass spectral analyses and has functioned as a Quality Control Coordinator on the previous contract.

#### 5.1.1 PEI Associates

Mr. Les Ungers will serve as Program Manager for PEI. Mr. Ungers is a certified industrial hygienist. His credentials were submitted in the proposal for this contract.

Mr. Tom Janszen, a biologist, will serve as the Work Assignment Leader for PEI. His credentials are contained in Appendix E.

Mr. Tom Wagner will serve as the Quality Assurance Manager and the Quality Assurance Coordinator. His credentials are contained in Appendix E.

Mr. Charles Zimmer will serve as Quality Control Coordinator for PEI. His credentials are contained in Appendix E.

## 5.2 Battelle Columbus Division

Dr. Jean Chesson will serve as the Battelle Program Manager and Task Leader. Her credentials can be found in the Battelle contract.

Ms. Ramona Mayer will serve as the Battelle Quality Assurance Administrator. Her credentials can be found in the Battelle contract.

Mr. Robert G. Heath will assist the work assignment leader. He is a senior biometrician with thirty years experience and managed the design and operation of several surveys and field studies. Mr. Heath is currently retired from government service and is employed as a consultant to Battelle.

# SECTION 6.0

## MIDWEST RESEARCH INSTITUTE'S FACILITIES, EQUIPMENT, CONSUMABLES AND SERVICES

### 6.1 Facilities

Sample preparation will be performed in MRI lab 315 W designated in part for this project. This laboratory is equipped with the fume hoods, and analytical balance and the volumetric glassware required to carry out this task. Mass spectral analyses and data processing will be performed in one of MRI's mass spectrometer facilities (MRI Lab 144N).

### 6.2 Equipment

The sampling equipment used on this task include:

1. 0.5 gal glass jugs with teflon lined caps
2. 0.5 Liter glass jars with teflon lined lids
3. Coolers
4. Clam rakes
5. Stainless steel sediment scoop
6. Floating platform (two canoes rafted together) for deep water sampling
7. Ekman dredge sampler
8. Kemmerer water column sampler
9. Hip waders
10. Transport vehicle with trailer hitch
11. 100 ft. tape measure and 6 ft. folding ruler
12. Strapping Tape
13. Thermometer
14. Bubble pack packaging material
15. MRI address labels
16. Topographic maps
17. Stopwatch, logbook, camera, indelible pens

The major piece of analytical equipment to be used on this project is a Finnigan 4000 Gas Chromatograph/ Mass Spectrometer system. This system is equipped with a fused silica capillary column, a negative chemical ionization source and a J & W on column injector. The system will be interfaced to an Incos 2400 data handling system.

The mass scale will be calibrated daily, in the negative ion mode, using perfluorotributyl amine (FC-43) prior to sample analysis. For reproducibility of the relative abundance measurements, the abundance ratio of the m/z 414: m/z 633 ions will be adjusted to 1:3 ( $\pm$ 10% ).

6.2.2 - Maintenance of the analytical equipment used in this task will be done according to manufacturers' specifications and at their recommended frequency. This is summarized in Table 6.1

6.3 Consumables

- 0.45 micron filters (Millipore)
- Hexane, non spectro grade (Burdick & Jackson)
- Iso-octane, high purity (Burdick & Jackson)
- Sulfuric acid, reagent grade (MCB)
- Sodium Sulfate, ACS reagent grade
- Alumina Woelm B, activity grade 1 (Woelm Pharma)
- Silica gel, chromatography grade

TABLE 6.1 MAINTENANCE

| Equipment | Service | Frequency |
|---|---|---|
| 1. Finnigan MAT 4000 : | | |
| | - change forepump oil | as needed |
| | - change differential pump oil | as needed |
| | - clean ion source | as needed |
| | - bake out vacuum chamber | as needed |
| | - repair electronic components | as needed |
| | - repair or replace jet separator | as needed |
| 2. Incos Data System: | - change air filter on disk drive | 6 months |
| | - align disk drives | as needed |
| | - repair or replace electronic components | as needed |

# SECTION 7.0

# EXPERIMENTAL DESIGN AND DATA GENERATION

## 7.0 INTRODUCTION

Chlorinated paraffins ($C_xH_{(2x-y2)}Cl_y$) have been reported to be toxic to mussels and rainbow trout at concentrations as low as a few parts per billion. Chlorinated paraffins are used in several commercial products primarily as lubricating oil additives (50% of total 1984 consumption).

There is little available information on levels of CPs in the environment. Only three previous studies have been obtained: two performed for Diamond Shamrock Corporation at Houston, Texas and the Grand River, Ohio and a third by ICI Limited at numerous sites in Great Britain [1,2,3].

While there is some debate over the precision of the analytical method used in these studies, they indicate that environmental levels are found in the parts per billion range in the water column and parts of per million range in sediment and biota. Also, these studies indicate that CPs are widely distributed in the environment. For instance, CPs were found in foods and human tissues and were detected upstream from any possible influence of a CP manufacturing plant.

Quantitation of CPs is complicated by the diverse nature of the structures and potential interferences from other organochlorine compounds. Commercial CPs consist of mixtures of linear saturated hydrocarbons with different chain lengths ($C_{10}$ to $C_{30}$), degrees of chlorination (30-70 percent), and distribution of chlorine atoms along the chain. Many positional isomers exist for each chemical formula.

The picture which emerges from these assessments is of a contaminant that historically has been difficult to measure analytically. Further, while believed to be transported to the environment primarily through the wastewater discharges associated with CP manufacturing and use in the lube oil industry, some data indicate that other transport mechanisms are possible.

We expect to find that due to its low aqueous solubility and low vapor pressure, CPs will be relatively chemically stable in the environment. Further, we expect to find that most CPs will rapidly adsorb to solids and settle to the substrate.

Extensive effort has been given to developing an analytical method capable of measuring these toxicants in different environmental matrices. A complete description of the analytical method of choice and its validation are provided in Appendices C and D.

## 7.1 Study Objective

The objective of this effort is to collect information that will help EPA determine, preliminarily, if chlorinated paraffins exist in the water environment ,i.e the water column (including suspended material), the sediment and in biological tissue and at what environmental levels. Because chlorinated paraffins are used predominantly in the lube oil business, this study is designed based on the assumption that if CPs exist in the aquatic environment, they will most likely be found in waters receiving discharge from CP manufacturers, processors of lubricating oils and users of these oils. Therefore, for the purposes of this study, a selection of these receiving waters will represent the water environment as expressed in the statement of objective. The first site to be addressed is a site receiving discharge from a CP manufacturer. The second site is a site representing a user of the lube oils.

## 7.2 Experimental Design

The experimental design for this study has necessarily been developed without the knowledge of the frequency of occurrence of residues in the study areas or the statistical parameters of such residues. The design has also been developed with the expectation that the precision and accuracy of the analytical method (concurrently being determined) will be acceptable. The design calls for the collection of water, sediment, and tissue samples from a specified number of sampling stations. These stations are deployed in the receiving water upstream of and downstream from an identified industrial discharge point and at designated locations within the plants' wastewater treatment processes.

The experimental design has been developed to meet the study objective of screening the specified aqueous environment for the presence of CP residues at the time of the individual field studies. As such, it is not a statistically-designed sample survey of CP residues in the designated watersheds.

The design allows for the data to be analyzed, at least initially, using non-parametric statistical methods. In particular, the data for each medium should lend itself to a Kruskel - Wallis one way analysis of variance to determine whether statistically significant differences exist among station residue levels. Other non-parametric measures of the consistency of results among data sets are possible [4].

All samples will be collected and handled using procedures fully approved by EPA.

The design calls for the collection of a minimum of three individual grab or composite samples of water and three individual grab or composite samples of sediment at specified locations (stations).

The design also calls for the collection of mussels, where available. It is anticipated that 8 to 10 small to medium mussel specimens will be required to compose a sample. Where mussels are not available, efforts will be made to collect invertebrate larval tissue. Fish may be collected if no other biota are available.

To enhance study efficiency snd minimize analytical costs, analyses will be conducted in a logical sequence of sets and subsets. Three sets are to be constructed such that the first set consists of the first samples of each type of medium collected at each of the designated stations, the second set comprises the second samples of each medium and so forth. Subsets comprise all samples of a given medium within a set. The decision to analyze a given set will depend on the analytical outcome of the previous sets. The order of analyses of subsets will be decided by the MRI analyst.

As a partial measure of method validity, QC field samples are included in this design. In addition to providing a measure of possible residue degradation during shipping and storage, these samples also provide limited measures of method precision, accuracy, and the probability of false negative outcomes. (See section 7.7).

This experimental design is translated to the Sugar Creek area in Appendix A; it is translated to the Tinkers Creek area in Appendix B.

7.3 Site Specific Sampling Plans.

- See Appendix A for the field sampling plan for Sugar Creek Dover, Ohio.
- See Appendix B for the field sampling plan for Tinkers Creek, Bedford, Ohio.

7.3.1 Water Column Data.

- Water Column samples will be limited by the field team's physical access to the stream.
- For shallow waters, collection will be achieved using a hand held, one half gallon glass jar. The jar will be submerged in the stream at mid-depth until all air is replaced by a water sample.
- For deep waters, collection will be achieved using a Kemmerer water sampler. These samples will be depth-integrated with collections made near the bottom, at mid-depth and near the surface.
- See Appendices A and B for more detail.

7.3.2 Suspended Solids Data.

The water samples will be filtered using a 0.45 micron Millipore filter and the suspended solid fraction extracted and analyzed separately.

7.3.3 Sediment Data

- Sediment samples will be limited by the field team's physical access to the stream.
- For shallow waters, collection will be achieved using a hand-held stainless steel scoop.
- For deeper waters, collection will be achieved using an Ekman dredge sampler.
- Sediment will be transferred to 500 ml. glass jars with teflon lined lids.
- See Appendices A and B for more detail.

7.3.4 Tissue from mussels will be collected using a hand-held "clam rake". Larval samples will be collected by dredging and sieving or manually by overturning rocks and rubble. Any fish collection will be done with nets.

### 7.3.5 Sample Preservation and Transportation

Field samples will require no preservative. All sample jars will be stored in coolers and out of direct sunlight. They will be transported in ice-filled coolers with sufficient packaging material to reduce the possibility of breakage. Any mussels collected during the field survey will also be placed in an ice-filled cooler. This is expected to help keep the mussels alive while being transported to the MRI laboratory in Kansas City, Missouri. Upon arrival at the MRI laboratory all unhealthy or dead mussels will be discarded before analysis. All water, sediment, and mussel samples will be shipped via commercial airlines or by overnight delivery service.

## 7.4 Field Quality Control

Monitoring of toxic substances requires special quality control procedures beyond those necessary for monitoring conventional parameters because toxicants generally occur in trace concentrations. The most up-to-date sampling and handling procedures recommended by EPA for a number of toxic and conventional parameters are detailed in a recent publication [5].

Monitoring for chlorinated paraffins requires even more demanding quality control procedures because of the potential for contamination. During this study special precautions will be made to avoid this contamination. These include: using polythene gloves in the field and in the laboratory to avoid possible contamination by the hands, avoiding seals and paints which may contain CPs and avoiding PVC and plastic materials which may contain CPs.

A Field Study Site Observation Sheet (Figure 7.2) will be filled out for each sampling station deployed in the field. The field study crew will use this sheet to describe each sampling station site, weather conditions, and the like. Also, for each sample collected at a station, the field study crew will fill out the information required on Sample Data Sheets (Figures 7.3 and 7.4). The field study crew will use these sheets to record sample information such as the time of collection, depth of sample collection and the like.

All samples will be uniquely identified with preprinted barcode labels. Additionally, a data base will be used to record each sample as it arrives in the lab and to track the samples. Data will also be recorded in laboratory notebooks on approved forms and on strip charts.

## 7.5 Sample Traceability

The MRI sample traceability protocol will be followed for sample tracking for this project. Traceability records will start with sample collection when samples are transferred to the laboratory by the completion of the lower portion of the Sample Data Sheets. The data base associated with the barcode traceability system will be used to record and monitor all sample transfers, all staff associated with transfers, and the date/time of all transfers.

### 7.5.1 Barcode labels

Uniquely numbered barcode labels (printed as a set of 6) will be used to physically track samples for this project. One of the labels will be affixed to the sample container; and a second will be affixed to a Sample Data Sheet. The remaining labels will be affixed to subsamples as needed.

## 7.6 Laboratory Analysis Procedures

See Appendix C for the analytical protocol. A flow chart of the steps involved in the analytical method is shown in Figure 7.5.

## 7.7 Quality Control Checks

Spiked water samples will be prepared at two stations in the Sugar Creek site(Stations B and L1) and two stations at the Tinkers Creek Site (Stations A and D). Water samples will be spiked at 50 ppb. The water sample collected from station L1 at the Sugar Creek site will be taken at mid-depth for spiking.

FIGURE 7.2 FIELD STUDY OBSERVATION SHEET

Site ID: _____ Date: _____ Time: _____

Signature: _____ Title: _____

Sampling Station Description: _____

_____

_____

_____

_____

_____

_____

Weather Conditions: _____

_____

_____

_____

Personal Observations: _____

_____

_____

_____

_____

_____

_____

Dover CP production during Field Study: _____ lbs.

FIGURE 7.3 SAMPLE DATA SHEET

| | | |
|---|---|---|
| Field Study: SUGAR CREEK DOVER, OHIO | Contract Number 68-02-4252 | Date (Mo/Da/Yr) |
| Station ID: | Work Assignment No. | Substance Monitored: Chlorinated Paraffin |
| Flow (cfs): Field: Calculated: | Samples collected by: | |

| Sample No. | Type of Sample 1 = water 2 = sediment 3 = mussel | Comp. or Grab | Temp. C° | Time | Depth (ft) | Remarks |
|---|---|---|---|---|---|---|
| | | | | | | |
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| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Samples relinquished to:_____ by:_____ on:_____ ( Date )

to:_____ by:_____ on:_____ ( Date )

FIGURE 7.4 SAMPLE DATA SHEET

| | | |
|---|---|---|
| Field Study: TINKERS CREEK BEDFORD, OHIO | Contract Number 68-02-4252 | Date (Mo/Da/Yr) |
| Station ID: | Work Assignment No. | Substance Monitored: Chlorinated Paraffin |
| Flow (cfs): Field: Calculated: | Samples collected by: | |

| Sample No. | Type of Sample 1 = water 2 = sediment 3 = larvae | Comp. or Grab | Temp. C° | Time | Depth (ft) | Remarks |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Samples relinquished to:_____ by:_____ on:_____ ( Date )

to:_____ by:_____ on:_____ ( Date )

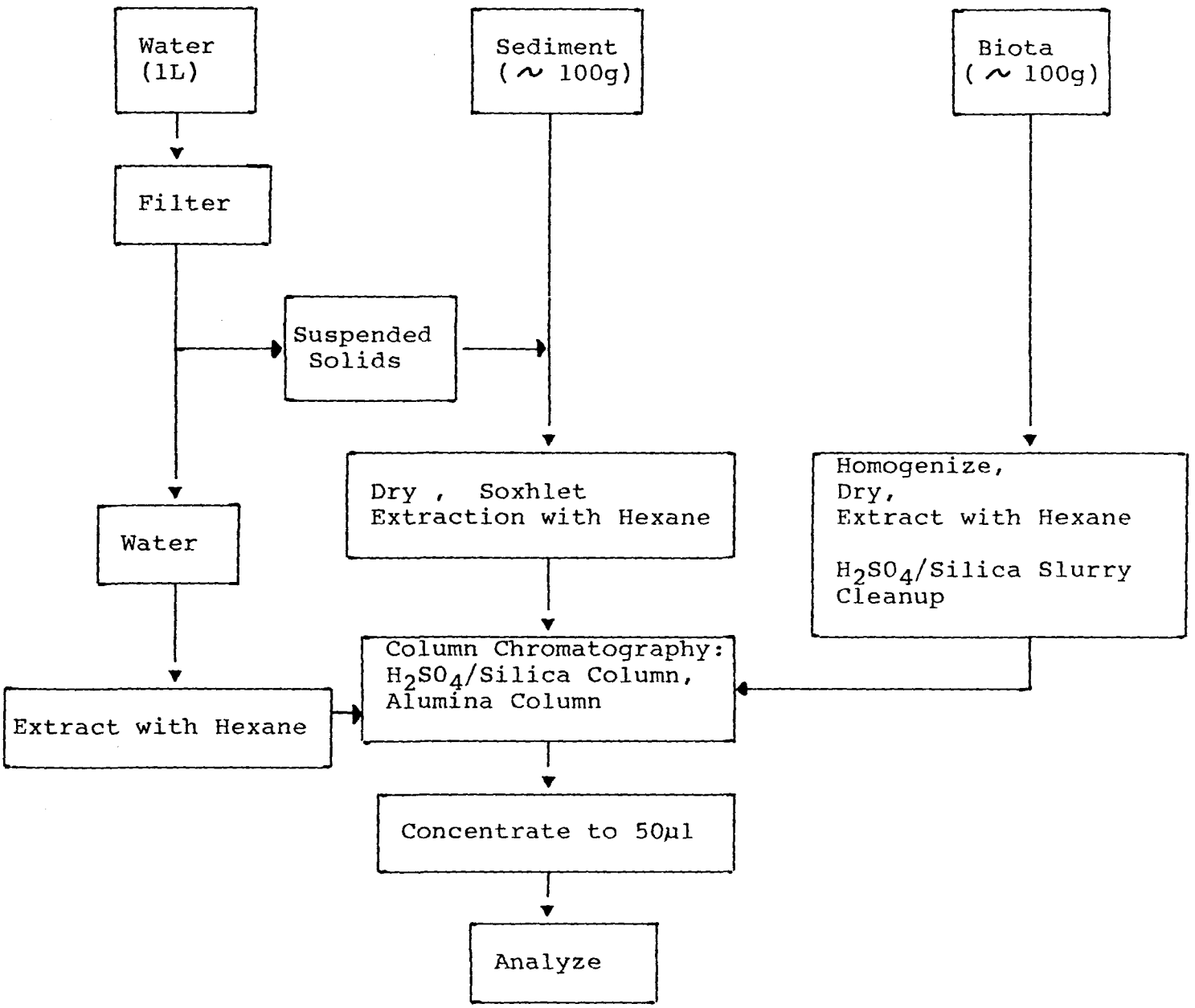



FIGURE 7.5 SCHEMATIC OF ANALYTICAL METHODS

These QC field samples will be collected in three 4-liter glass jugs and transferred to one-half gallon glass jugs for spiking. Separate sets of 4 liter jugs will be provided for stations B and L1. Homogenization and spiking will be done according to the following procedure.

The four liter glass jugs will be pre-marked in the laboratory at the 3-liter level. The one-half gallon jugs will be pre-marked in the lab at the 475, 950, and 1425 mL levels. In the field, the 4-liter jugs will be filled to the marks (3L) with water sample. The first jug will be shaken thoroughly and the contents poured into the one-half gallon jugs to the first mark (475 mL). The second and third 4-liter jugs will be used to fill the one-half gallon jugs to the second and third marks respectively. Two of the four samples for each station will be spiked at the 50 ppb level. This will be done by adding 1.0 mL of a chloroparaffin standard (approximately 70 ug/mL each cell) in methanol. The remaining field QC samples will be spiked at the same level after they are returned to the laboratory.

Extraction and analysis of the 8 QC samples (4 samples from each of two stations), constituting 16 analyses (8 filtrate and 8 suspended solids fractions) will be done at the same time the field samples are analyzed (see Appendix A, Table 5 and Appendix B, Table 5)

In addition to these field QC samples, trip QC samples will be prepared as follows:

Two samples of laboratory deionized water (volume = 1425 Ml) will be prepared for each of the four QC stations, i.e. stations L1 and B (Sugar Cr.) and stations A and D (Tinkers Cr.). These samples will then be transported to the field. At each of the designated QC stations a set of two of these samples will be removed from the cooler and one of these per QC station will be selected, at random, and spiked at 50 ppb (a total of 4 samples). The other sample from each set of two will be returned to the laboratory and analyzed along with its spiked counterpart (a total of 4 samples).

Just prior to analysis, an additional sample per QC station (a total of 4 samples) will be prepared, again using laboratory deionized water, and spiked at 50 ppb.

Because the rate of adsorption of CPs to suspended solids may differ between environmental and spiked samples and between field-spiked and laboratory-spiked

samples, CP recovery will be expressed in a weight/volume basis (ug/l) after summing the weights of CP in the filtered water sample and its respective solids. (It is similarly meaningful to express CP residues in water samples in the same way, especially when comparing residues in samples containing different amounts of suspended solids. For example, residue levels in the solids of two samples might be quite similar on a weight CP/weight solids basis, whereas total weight of CP would be considerably greater in the water sample having the higher concentrations of suspended solids).

7.7.1 General

New lots of reagents are checked prior to use, or current lots of reagents are checked when method blank problems are experienced.

7.7.2 The control checks that will be utilized are the following:

Performance Sample: Prior to sample analysis

Method Blanks: One per sample batch analyzed

Daily Standards: One before and after sample analysis for precision and accuracy as described in Section 9.0.

7.7.3 Calibration

The GC/MS system will be calibrated prior to sample analysis over a range which covers the sample concentrations. The initial validation will be checked daily with a midpoint calibration standard at the beginning of the sample run.

7.7.4 Definitions

7.7.4.1 Method Blanks: Procedural blanks are carried through the entire procedure to check for contamination. These will consist of distilled water for water field samples, sodium sulfate for sediment and mussels, and blank filters for suspended solids.

## 7.8 MRI Systems and Performance Audits

7.8.1 Systems Audits: Systems audits by the QCC/QAC shall include:

- Inspecting facilities and equipment for adequacy, appropriateness, and safety during use.
- Reviewing actual practices versus written procedures and protocols.
- Inspecting the records of maintenance and calibration.
- Inspecting QC practices.
- Assisting/conducting data audit prior to report submittal.
- Preparing and submitting a report with recommended corrective actions to the QAM, and after approval, to the work assignment leader and program manager.
- Conduct additional audits as directed by the QAC/QAM.
- Assisting/preparing QA report for the EPA's work assignment manager.

### 7.8.2 Analytical Performance Audits

The performance audit sample is designed to check the operation of the analytical equipment. Several blind performance samples will be independently prepared by the QCC and submitted for analysis before and during the analysis of the reqular samples. Performance audit samples will also be analyzed if (1) the QCC/QAC believes the analysis procedure has changed, (2) analytical problems are suspected, or (3) the MRI work assignment leader or the EPA work assignment manager requests samples. All audit findings will be reported to the project leader and program management by the QAM. A summary of the audits will be provided to the EPA work assignment manager.

### 7.8.3 Field Performance Audit

A Battelle representative will be in the field to ensure compliance with the sampling protocol and will write a trip report.

### 7.8.4 QAC/QAM Audits

Additional audits will be conducted or directed by the QAC/QAM as follows:

- Schedule and conduct additional audits as needed, e.g., staff credentials, quality control data and practices.

- Review and approve the report and supporting evidence for accuracy and QA compliance prior to report submittal to EPA.

SECTION 8.0

# DATA PROCESSING

## 8.1 Collection

Data collection by MRI will utilize both manual and computerized acquisition systems. All activities shall be legibly recorded using permanent ink in the project notebook or on worksheets. Each person who records data shall sign and date each sheet. Strip charts, magnetic tapes, etc., shall be labeled with a format identifier, project number, date, the ID(s) of the instrument, and the name of the person responsible for the data. Custody of the original data media will be the responsibility of assigned project staff until archived.

## 8.2 Data Reduction

Standard data reduction procedures with built-in checks will be used. For example, if an integrator or computer is used to calculate concentrations, the standards used to generate the curve must be back-calculated using the curve to ensure satisfactory curve fitting over the anticipated range. In addition, all sample manipulations (e.g., weighing, dilution, concentration, etc.) must be clearly documented.

## 8.3 Data Validation

The MRI work assignment leader will be responsible for assuring data validity which will include:

- Validating all equations and computer programs and documenting the validation.
- Validating and checking electronic data transfer.
- Proofreading manual data transfers.
- Screening data for consistency by a second project staff member.
- Checking calculations.
- Performing outlier checks.

- Examining QC data and QC checks.
- Maintaining records of reviewing, proofing, and validation.
- Examining data/information for completeness, representativeness, and comparability.

## 8.4 Storage

Original data will be documented in laboratory notebooks, on printed paper, as strip chart recordings, or or magnetic tape or disk. Permanent storage of work assignment data in the formal project file and hard copy from magnetic media will be archived (SOP-QA7). The storage location of magnetic media will be reported.

## 8.5 Data Analysis

MRI will provide a copy of final analytical data, QC data, and chronological order of analysis to Battelle Columbus Division for statistical analysis. Included in the report will be all protocol deviations and assumptions. Battelle will provide statistical analysis of these data.

## 8.6 Results and Conclusions

Battelle will develop the results and conclusions based on the analyses of the data. This should include a discussion of the limits and appropriate uses of the data and possible uses of the data which are not statistically supportable.

# SECTION 9.0

## DATA QUALITY ASSESSMENT (OBJECTIVES)

The objectives for instrument precision and accuracy are 30% instrument precision (stability) over an analysis period and 100 ± 10% accuracy for the daily calibration check.

The objective of precision for this method will be to obtain chloroparaffin concentrations for replicate spike samples which have range percent of less than 30% of each other. The objective for accuracy will be to obtain chloroparaffin concentrations which have percent difference of less than 30% of the actual chloroparaffin concentrations. Average recovery efficiencies for chloroparaffins using spiked matrices should fall within the range of 70-130% to yield meaningful data.

These precision, accuracy and recovery values will be obtained from the validation work which in turn will be based upon the experimental design.

### 9.1 Analytical Precision

Precision is determined by performing replicate analysis. For data sets with a small number of points ($2 < n < 8$), the estimate of precision will be expressed as range percent (R%).

$$R\% = \frac{x_1 - x_2}{\overline{X}} \times 100$$

Where $X_1$ = highest concentration value determined
$X_2$ = lowest concentration value determined

$\overline{X}$ = mean concentration value of the set

and

$$\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n}$$

Where $X_i$ =ith determination
$n$ = number of determinations.

The detection limit (EDL) for the analytical system will be defined as three times the signal to noise level of the analytical instrument.

The limit of quantitation (LOQ) for the analytical system will be defined as ten times the signal to noise level of the analytical instrument.

As an alternative, the estimate of precision may be expressed as percent relative standard deviation (% RSD):

$$R.S.D. = \frac{\sqrt{\dfrac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}}}{\bar{X}} \times 100$$

Where n = number of replicate determinations.

$$\bar{X} = \text{mean} = \frac{\sum_{i=1}^{n} Xi}{n}$$

The precision of the analytical system, which includes instrument stability during analysis, will be monitored by analyzing the midpoint standard at the beginning and end of each day's analysis and plotted on a control chart.

## 9.2 Accuracy

The accuracy (A%) of the analytical method will be established by performance samples and the daily midpoint standards. The initial daily midpoint standard will be plotted on control charts and monitored.

$$A\% = \frac{F}{A} \times 100$$

Where F = found weight or concentration of chemical
A = actual weight or concentration of chemical

## 9.3 Recovery

Recovery (RE%) will be calculated from the results of the spiked sample and unspiked sample analyses.

$$RE\ (\%) = \frac{S - U}{A} \times 100$$

Where, S = concentration of the spiked sample
U = concentration of the unspiked sample
A = concentration of the added standard

## 9.4 Traceability of Instrumentation

All collection and measuring instrumentation will have a unique identification number. Maintenance/calibration and use logs will be maintained.

## 9.5 Traceability of Samples

All samples will have a unique identification number along with information on field site, monitoring location, collection device, etc. The samples will be labeled with adhesive bar code labels to identify the samples and trace them through the sampling and analytical procedures.

## 9.6 Traceability of Data

Data will be documented and filed to allow complete reconstruction from initial field records to data archiving.

## 9.7 Completeness

Due to the variety of data points available per field test site, every effort will be made to maintain a level of data completeness that will assure meaningful data. Data completeness (C%) will be determined from the number of values which fall within the instrument accuracy and precision objectives:

$$C\% = \frac{\text{Number of acceptable values}}{\text{Total number of values}} \times 100$$

# CORRECTIVE ACTION

## Midwest Research Institute

For those subtasks performed by MRI, the MRI work assignment leader has primary responsibility for taking corrective action; if he is unavailable, the program manager, and/or the QAC/QAM shall be contacted for instructions. Some of the types of problems and corrective actions to be taken are listed below. Unresolved problems are reported by the QAM to the Associate Director of K.C. Operations and to the Senior Vice President for resolution.

## 10.1 Performance/Systems Audits

If problems are detected during an audit:

- The auditor shall notify the person responsible, the work assignment leader, and the QAC/QAM of the problem(s) and any action(s) he has taken.
- The work assignment leader and the person responsible shall correct the problem, then notify the QAC/QAM.
- The auditor shall then prepare, and after QAC/QAM approval, send a problem/action taken memo to the program manager and the work assignment leader.

## 10.2 Loss of Data

The work assignment leader shall investigate the problem then perform one of more of the following actions:

- If the problem is limited in scope, the problem/action taken is documented in the notebook; the work assignment leader then prepares and sends a problem/action memo to the QAC/QAM, and the program manager.
- If a large quantity of data is affected, the problem/action taken is documented in the notebook; the work assignment leader then prepares and sends a problem/action memo to the QAC/QAM, project manager, and the EPA work assignment manager.

## 10.3 Significant QA Problems

In general, the work assignment leader shall identify technical problems.

- The work assignment leader prepares and sends a problem memo to the QAC/QAM and program manager; if the problems are significant, the action is determined collectively.
- The action taken is documented in the notebook.
- The problem and action taken is reported to the EPA work assignment manager.

## PEI Associates

For the subtasks performed by PEI Associates, the PEI work assignment leader has primary responsibility for taking corrective action. If he is unavailable, the PEI Program Manager, and/or the QAM/QAC shall be contacted for instructions. Some of the types of problems and corrective actions to be taken are listed below. Unresolved problems are reported by the QAM to the PEI Associates Director for resolution. All corrective actions should be reported to MRI.

## 10.3 Loss of samples

The work assignment leader shall investigate the problem and then perform one or more of the following actions:

- If the problem is limited in scope, the problem/action taken is documented in the notebook. The work assignment leader then prepares and sends a problem/action memo to the QAM/QAC and the Program Manager.
- If a large quantity of data is affected, the problem/action taken is documented in the notebook. The work assignment leader then prepares and sends a problem/action memo to the QAM/QAC, Program Manager, and the EPA Work Assignment Manager.

## 10.4 Significant QA Problems

In general, the Work Assignment Leader shall identify technical problems.

- The Work Assignment Leader prepares and sends a problem memo to the QAM/QAC and Program Manager. If the problems are

significant, the action is determined collectively.

- The action taken is documented in the notebook.
- The problem and action taken are reported to the MRI Work Assignment Manager.

Battelle Memorial Institute

For the subtasks performed by Battelle Columbus Division, the Battelle Work Assignment Leader has primary responsibility for taking corrective action. If he is unavailable, the Program Manager, and/or the QAA shall be contacted for instructions.

In general, the Work Assignment Leader shall identify technical problems.

The Work Assignment Leader prepares and sends a memorandum to the Program Manager and the QAA. If the problems are significant, the action is determined collectively.

The action taken is documented. The problem and action taken are reported to the EPA Work Assignment Leader.

# SECTION 11.0

# DOCUMENTATION AND REPORTING

## 11.1 Documentation

- Original (raw) documentation shall be recorded in permanent ink.
- A hard copy of original computerized data, which is reported, will serve as the official copy.
- Initials may be used in place of signatures if they are readily traceable.
- Manual corrections of original data will be performed as follows: Draw a single line through the incorrect entry so that the original entry remains legible. Add the correct entry; then explain, initial, and date the correction.
- New information may be added to original data if it is initialed and dated.
- All deviations from standard operating procedures (SOPs), procedures, and protocols will be documented.
- Assumptions will be documented.
- Strip charts, magnetic tapes, etc., will be labeled with a format identifier, the date, the ID(s) of the sampling equipment, and the name of the person responsible for the data recording equipment.

## 11.2 Document Control

- Original sampling data will be documented and stored in laboratory notebooks, approved forms, on printer paper, on magnetic tape, and as strip chart recordings.
- The location of all original data will be documented by the work assignment manager until the files are archived.

## 11.3 QA Reports to Management

The QAC/QAM, in cooperation with the work assignment leader, shall identify critical phases of the project which will be subject to inspection. The inspection will include a review of:

- Staff credentials.
- Equipment maintenance and calibration records.
- Equipment performance.
- Documentation practices.
- Recordkeeping practices.
- Adherence to protocols, SOPs, and QA plan.
- Assessment of data accuracy, precision, and completeness.

The results of inspections and audits will be reported quarterly by the QAM to Program MRI management; summaries will be reported to the EPA work assignment manager.

## 11.4 Report Design

Progress, interim draft final, final reports, and QA summary reports will be submitted in accordance with the provisions for reporting in the contract. Verbal status reports will be made biweekly to the EPA work assignment manager.

SECTION 12.0

REFERENCES

1. Campbell, Ian and George McConnell. 1980. Chlorinated Paraffins and the Environment. 1. Environmental Science and Technology, Vol. 14, Number 10, October 1980.

2. Letter from Alan E. Ramm to Jack Borror dated 11-21-78 concerning sediment and biota sampling.

3. Letter from Alan E. Ramm to Jack Borror dated 7-19-77 concerning results of Chlorowax investigations in Grand River.

4. Segal, S., Non-parametric Statistics, 1956, McGraw-Hill.

5. U.S. Environmental Protection Agency, 1982, Test Methods - Technical Additions to Methods for Chemical Analysis of Water and Wastes. Office of Research and Development, Cincinnati, Ohio, EPA 600/4 - 82-055, December 1982.

# APPENDIX A

## FIELD STUDY DESIGN AND SAMPLING PROTOCOL

## FOR

## SUGAR CREEK

## DOVER, OHIO

# APPENDIX A - TABLE OF CONTENTS


| Section | Heading | Revision | Date |
|---|---|---|---|
| 1.0 | Description of the Study Area | | 9/12/86 |
| 2.0 | Waste Inputs | | 9/12/86 |
| 3.0 | Reconnaissance Survey | | 9/12/86 |
| 4.0 | Field Study Design | | 9/12/86 |
| 5.0 | References | | 9/12/86 |

## 1.0 Description of the Study Area

Sugar Creek is located in east central Ohio. From its source in Wayne County near Wooster, Ohio, it flows south, southeast toward its confluence with the Tuscarawas River. Near Beach City, Ohio, Sugar Creek is impounded; here it recharges the aquifer supplying the city of Canton's well field.

The drainage basin of Sugar Creek is largely rural. It is classified by the Ohio EPA as a warm water habitat. The focus of this field study is on the lower 4 miles of Sugar Creek from below Strasburg to the mouth. A map/schematic of this segment of Sugar Creek is given in Figure 1.1.

According to the 1986 State of Ohio Section 305(b) report [1] chemical/physical and biological conditions measured in the lower 4 miles of Sugar Creek in 1983 were generally good. Dissolved oxygen, conductivity, ammonia-N and nutrient concentrations were not indicative of any stress from sewage or other oxygen demanding wastes. Numerous pollution sensitive macroinvertebrates were collected at RM 1.8, and fish community health was good at two sites (RM 3.6 and 0.2). The chemical data did reveal a transient influence from acid mine drainage when runoff from small tributaries to lower Sugar Creek occurred during low stream flow in Sugar Creek. The water quality measured in the mainstem was not severly degraded during these events, and it is unlikely that chemical perturbations reached problematic magnitudes or frequencies based upon the relatively healthy benthos and fish faunas collected in Sugar Creek. However, *Ceriodaphnia* bioassays of Sugar Creek water collected at river mile (RM) 1.8 (immediately downstream from Goettge Run) did show reduced production of young. These findings combined with a reduction in sensitive macroinvertebrate species collected at RM 0.6 suggest the possibility of localized chronic pollution stress from acid mine drainage in lower Sugar Creek. It is likely that Goettge Run and the other small tributaries to Sugar Creek between the Beach City dam and the Tuscarawas River are impacted by abandoned strip mine land and may not be attaining their potential aquatic life uses (Ohio EPA 1986).

The Ohio Department of Natural Resources reported two fish kill incidents in 1983 and 1984 in Sugar Creek. Also, Twenty-one wild animals died as a result of unknown causes.

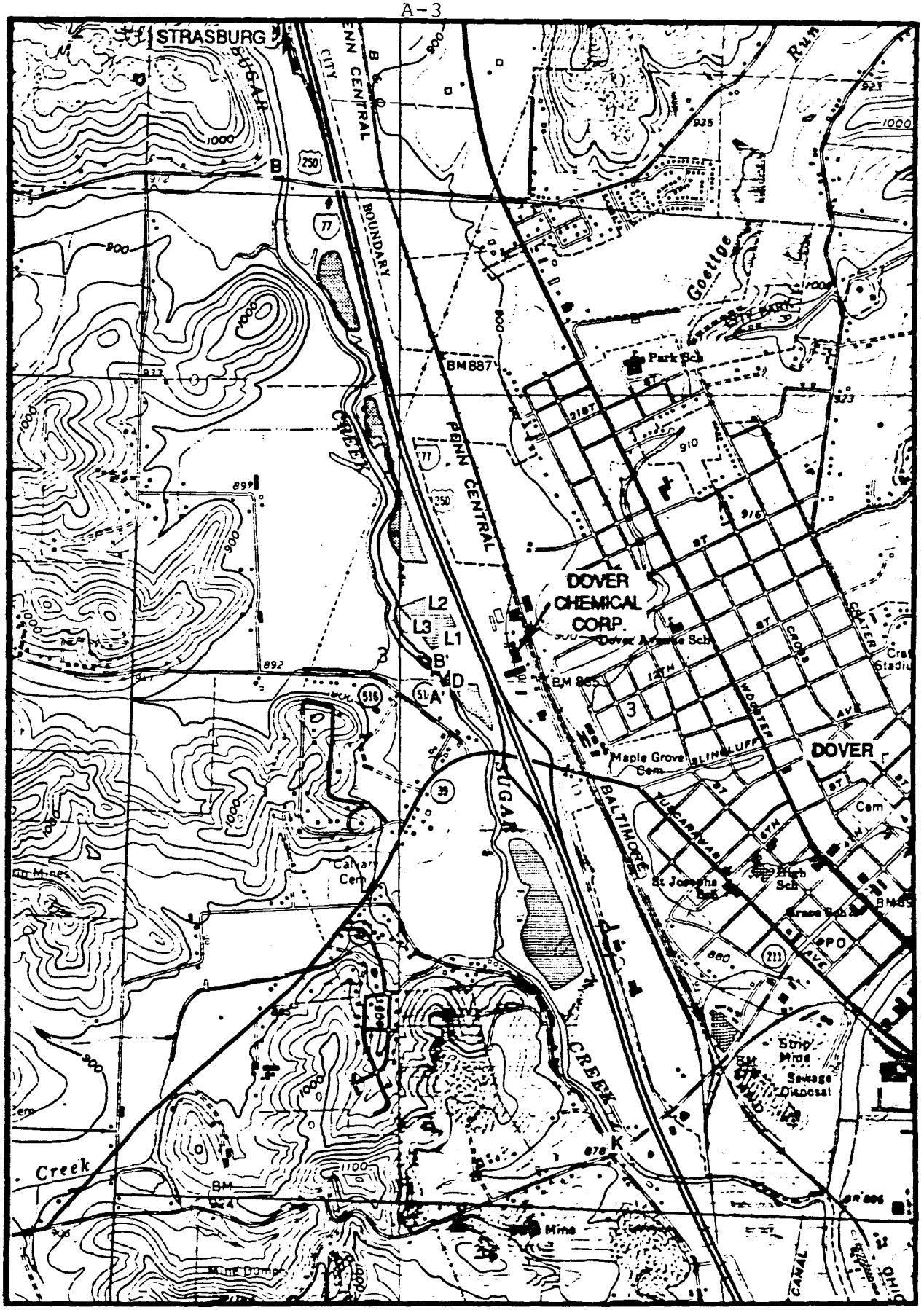



FIGURE 1-1 SUGAR CREEK STUDY AREA

The mean annual stream flow for this segment of Sugar Creek is approximately 330 cfs. Low flow for the area is approximately 30-50 cfs. Sugar Creek is about 50-75 feet wide and averages 1-2 feet in depth throughout this segment of the river. As it approaches its confluence with the Tuscarawas River, its depth increases to 8 feet. A variety of fish and macroinvertebrates are reported to populate the area. The creek bottom is a combination of gravel and sand. Access to the creek is limited. There are no public water intakes along this stretch of Sugar Creek.

## 2.0 Waste Inputs

The only point source discharges to this segment of Sugar Creek are from Dover Chemical Plant (RM 1.8) and the City of Strasburg wastewater treatment plant (RM 7.3). Acid mine drainage from Goettge Run (RM 1.8) is a principal nonpoint source of pollution.

## 2.1 Dover Chemical Corporation

Dover Chemical Corporation is the outfall of interest to this study. Dover Chemical Corporation is a major manufacturer of chlorinated paraffins, producing 21% of the total U.S. production.

Dover Chemical is located at 15th and Davis Streets in Dover, Ohio. At present Dover Chemical continuously pumps approximately 2.2 mgd of water from 2 of their 4 wells and discharges 1.6-1.8 mgd of water.

The 1980 production outputs for Dover Chemical are as follows:

| Product and By-Product | Annual Quantity |
|---|---|
| Chlorinated paraffins (liquid) | 6,100 tons |
| Chlorinated paraffins (resin) | 5,100 tons |
| Hydrochloric Acid | 18,000 tons |
| Sodium Hypochlorite | 2,766 tons. |

The Standard Industrial Code (SIC) for Dover Chemical is 2861.

The Dover Chemical plant employs about 90 people and is currently operating 24 hours a day 10 days on and 4 days off.

### 2.1.1 Chlorinated Paraffins Process Description

At the Dover Chemical plant chlorine gas and paraffin is continuously reacted to form the chlorinated paraffin. Sometimes carbon tetrachloride is used in this process as a solvent, or to remove free chlorine from solution. After the chlorine and paraffin is reacted it is passed through a degasser to vaporize the carbon tetrachloride. The carbon tetrachloride is then condensed and reused while the freed chlorine is used to produce sodium hypochlorite. After the chlorinated paraffin has passed through the degasser it is deposited on a conveyor belt for water cooling with well water until hardened. When it is solidified the chlorinated paraffin resin is ground, screened, and stored for sale.

Two dry dust collectors are used to collect the resin dust from the grinding operation, and are sold for use in making resin. The water used for cooling is sent to their treatment system. When the cooling water is sprayed against the underside of the conveyor belt to cool the paraffin product on top of the belt, it is likely that some water contact with the product or product residue may occur.

Liquid chlorinated paraffins are manufactured in a batch-reaction kettle. After reaction the chlorinated paraffins are sent through a degasser for removal of free chlorine gas from solution vessels and used to make muriatic acid (HCl). The other product of this reaction is chlorine gas which is used to make sodium hypochloride (bleach). Sometimes the concentrations of both by-product's gasses are too low to form their end products and are water scrubbed. This scrubbing water is then sent to the water treatment system.

A typical process flow diagram for the manufacture of chlorinated paraffins is shown in Figure 2.1.

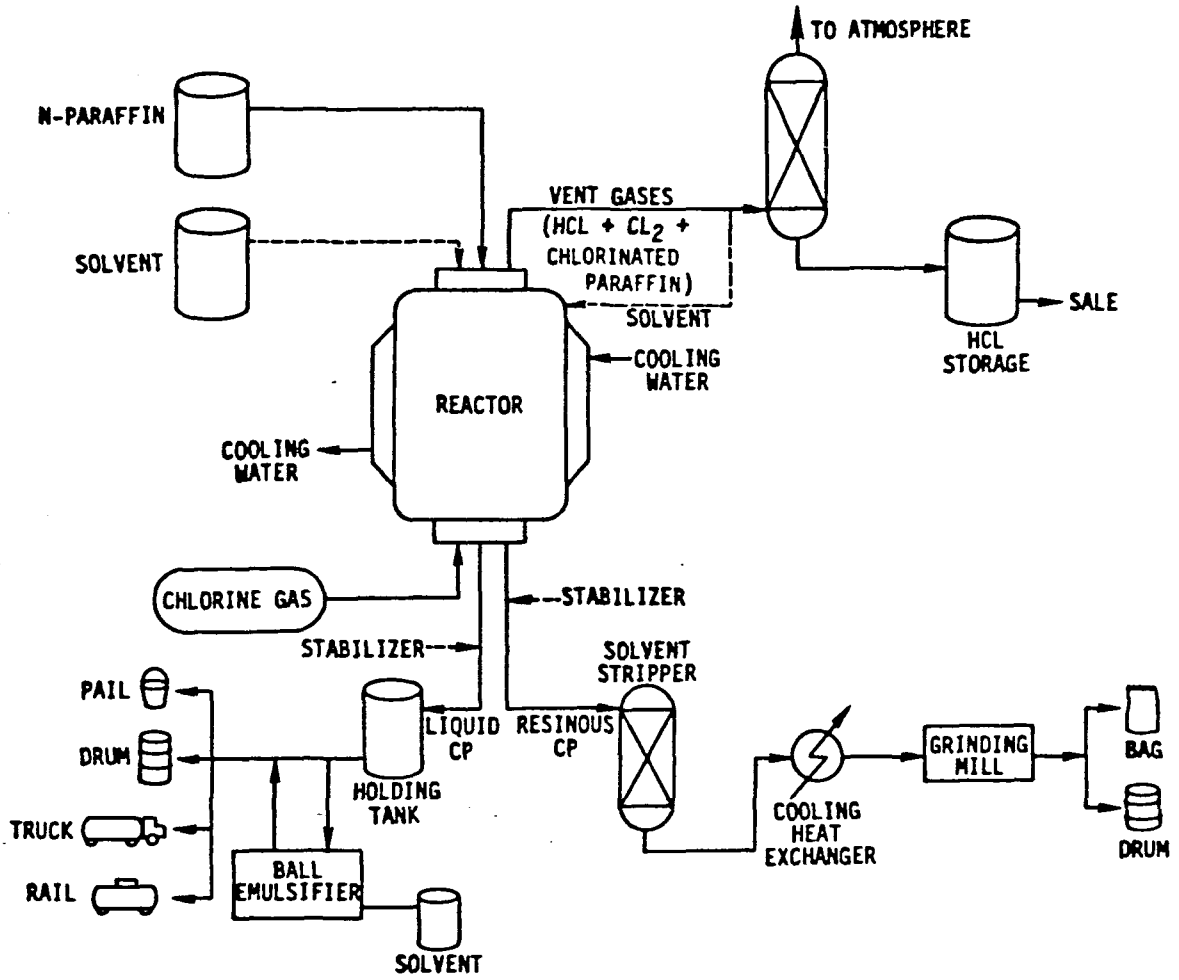



Figure 2.1. Process flow diagram for the manufacture of chlorinated paraffins.

Source PEI 1984

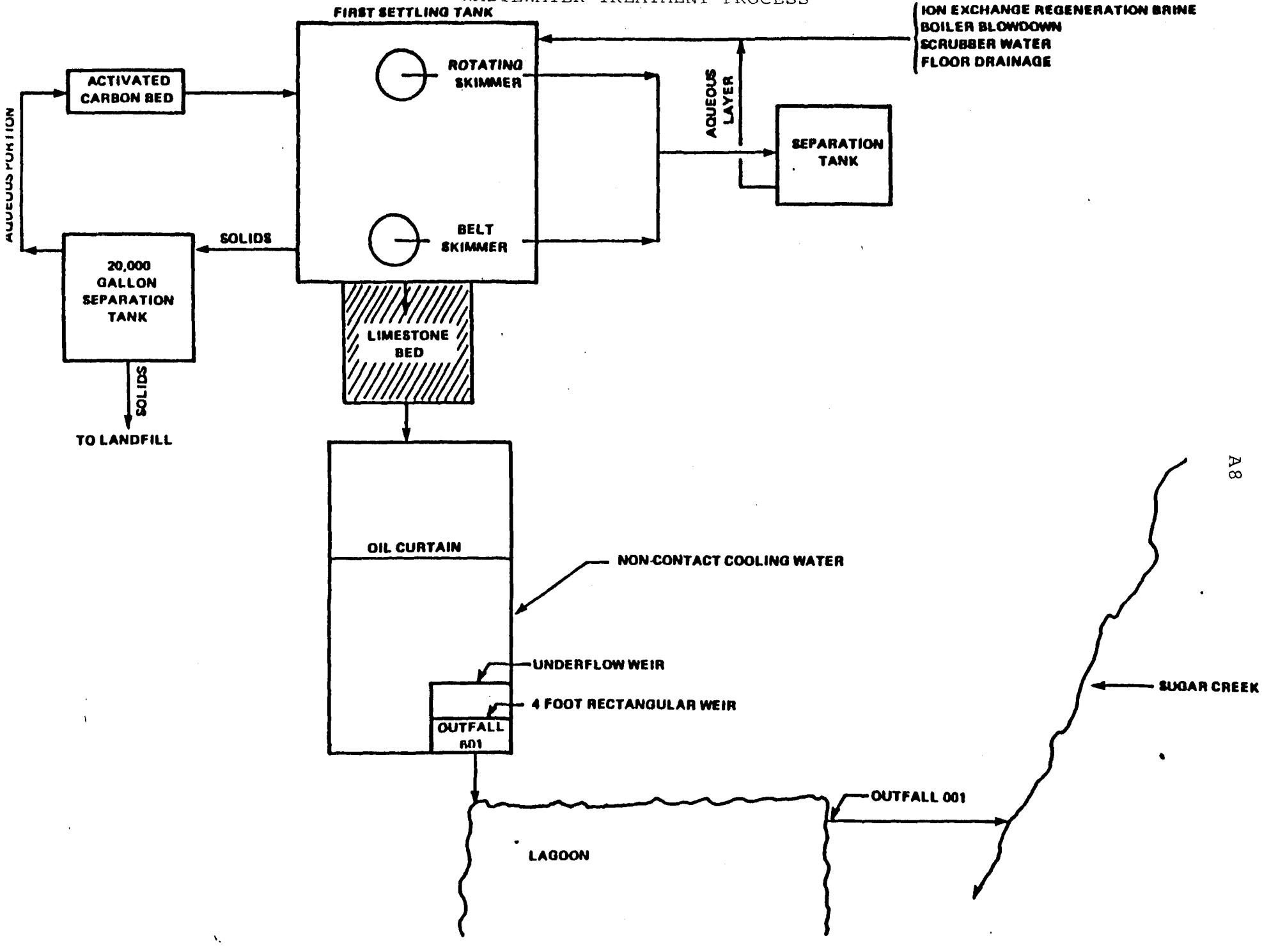
### 2.1.2 Dover Chemical Wastewater Treatment Process

Wastewater consists of non-contact cooling water, boiler blowdown ion exchange regenerant (deionizer for boiler makeup water), scrubber water and floor drainage. All wastewaters with the exception of non-contact cooling water enters a 10,000 gallon settling tank and overflows to a limestone bed for neutralization. This first settling tank is equipped with both a rotating oil skimmer and a continuous belt skimmer. Oil and grease accumulated by the skimmers is transferred to a separation tank. The aqueous portion is returned to the first settling tank. Solids from the first tank are pumped to a 20,000 gallon tank for further separation. This tank is occasionally drained of the aqueous layer which is subsequently passed through an activated carbon bed prior to pumping to the first settling tank. Water passing through the limestone bed flows to the second settling tank which is equipped with an oil boom and underflow weir prior to discharging over a four foot rectangular weir with end contractions. Non-contact cooling water enters the second settling tank. The point just after this weir is designated outfall 601. The discharge flows several yards through a pipe before it is discharged into a narrow canal. This canal then carries the wastewater to a lagoon. Discharge from the lagoon flows through a small unnamed ditch via outfall 001 and then to Sugar Creek.

The Dover chemical surface impoundment lagoon is owned by the company. It contains a captive population of fish, frogs and turtles. The impoundment has been known to overflow; however, no incidents have occurred in the past 2 years. The impoundment is approximately 9 acres in area and is more than 30 feet deep in places.

A simple schematic of the Dover Chemical Wastewater Treatment Process is given in Figure 2.2.

WASTEWATER TREATMENT PROCESS

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## 3.0 Reconnaissance Survey

On August 12 and 13, 1986 MRI and PEI personnel and Robert Heath, consultant to Battelle Memorial Institute conducted a reconnaissance survey of the Sugar Creek area. The objectives of this reconnaissance visit were twofold: (1) to collect field samples to test the analytical method for CPs developed and enhanced by MRI in order to estimate its recovery efficiency and precision and (2) to study the Sugar Creek/Dover area in preparing the final study design for the monitoring study in this area.

In support of the first objective, water and sediment samples were collected from three sites (stations) in Sugar Creek.

- Site A - Downstream from Dover Chemical at Tuscarawas Road.
- Site B - Under the bridge which carries the road to Winfield, upstream of Dover Chemical.
- Site K - Route 39 downstream from Site A, just above the confluence with the Tuscarawas River.

Sufficient water and sediment samples were collected to allow for a series of analyses aimed at validating the analytical method (See Appendix D). Mussels were not collected due to the lack of a permit. A short follow-up visit will be made to collect mussel samples.

In support of the second objective, the team was able to meet and discuss the area with EPA State personnel, visit and walk the Sugar Creek, and visit and walk the Dover Plant itself. Permission was granted by Dover Chemical Plant personnel to collect whatever samples from their plant necessary for the study. They only requested that samples collected be split and shared with Dover Chemical and that any photographs taken be made available to Dover Chemical. Several photographs of the area were taken and are available under separate cover.

## 4.0 FIELD STUDY DESIGN

The design for this study has necessarily been developed without the knowledge of the frequency of occurrence of residues in the study area(s) or the statistical parameters of such residues. The design has also been developed with the expectation that the precision and accuracy of the analytical method (which is concurrently being determined) will be acceptable.

The design calls for a total of eight (8) sampling stations; four stations in Sugar Creek and four in the discharge waterway: The station locations are shown in Figures 4.1, 4.2 and 4.3.

| Station ID | Location |
|---|---|
| L1 | In the Dover Chemical Plant settling lagoon near the lagoon's effluent. |
| L2 | In the Dover Chemical Plant settling lagoon near the influent from the plant discharge. |
| L3 | In the Dover Chemical Plant settling lagoon near the middle of the lagoon. |
| D | In the lagoon discharge ditch immediately above the point of discharge into Sugar Cr. |
| B | Sugar Creek under road to Winfield |
| B' | Sugar Creek just upstream of the Dover Chemical Discharge ditch. |
| A' | Sugar Creek just downstream from the Dover Plant discharge ditch but upstream of Goettge Run. |
| K | Downstream from the Dover Plant discharge and just upstream of the confluence of Sugar Creek and the Tuscarawas River. |

The design requires the collection of a minimum of three individual grab or composite water and sediment samples at each of the eight stations. It also calls for the collection of mussels at all four Sugar Creek stations. While mussels are not expected to habitate the lagoon or the drainage ditch, mussel samples will be collected at these stations, if possible. As mentioned, each mussel sample is a composite of the flesh of 8 to 10 individual specimens. The samples and analyses comprising each set are shown in Tables 1 through 4.

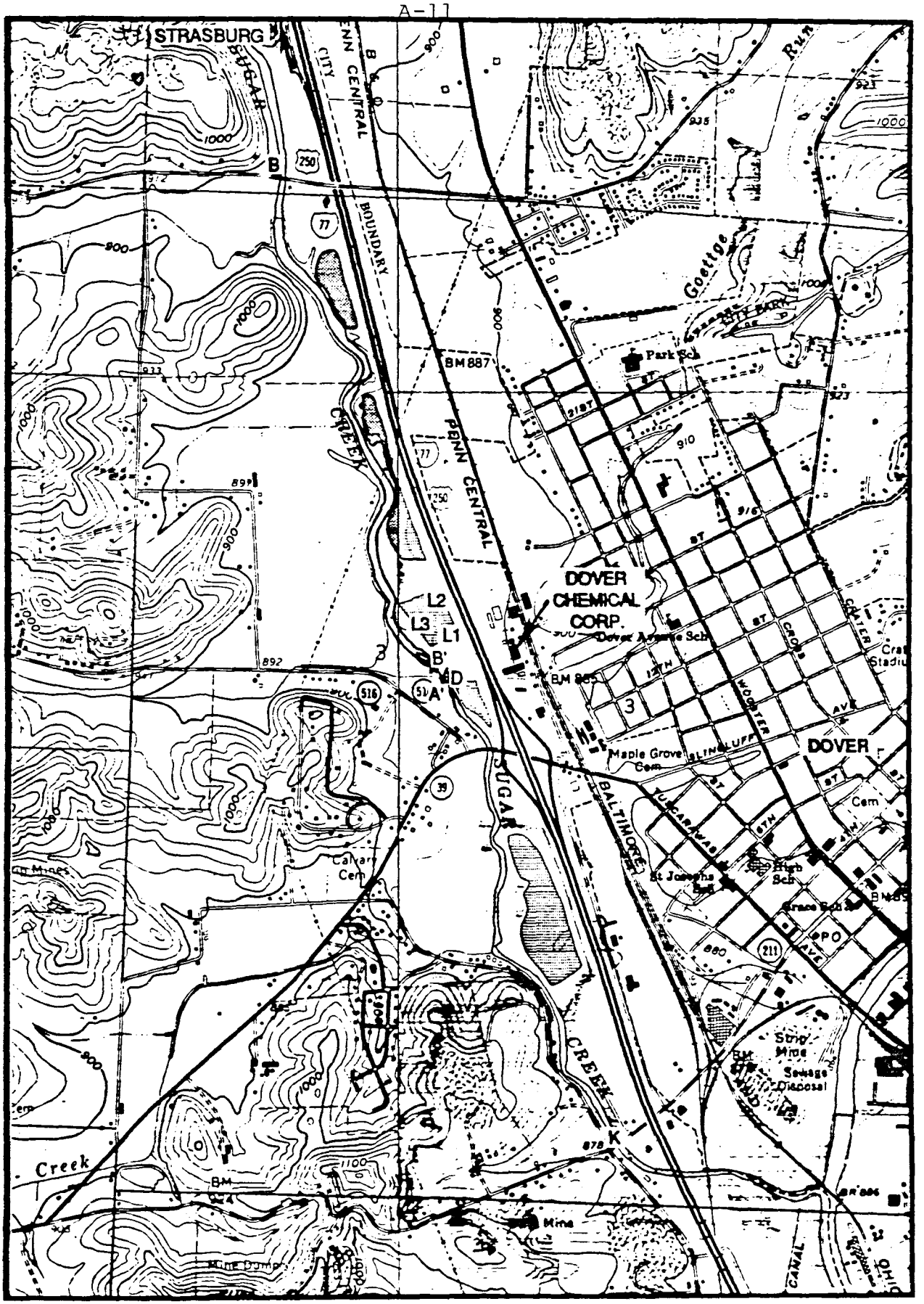



FIGURE 4.1 Locations of sampling sites at Dover Chemical and in Sugar Creek.

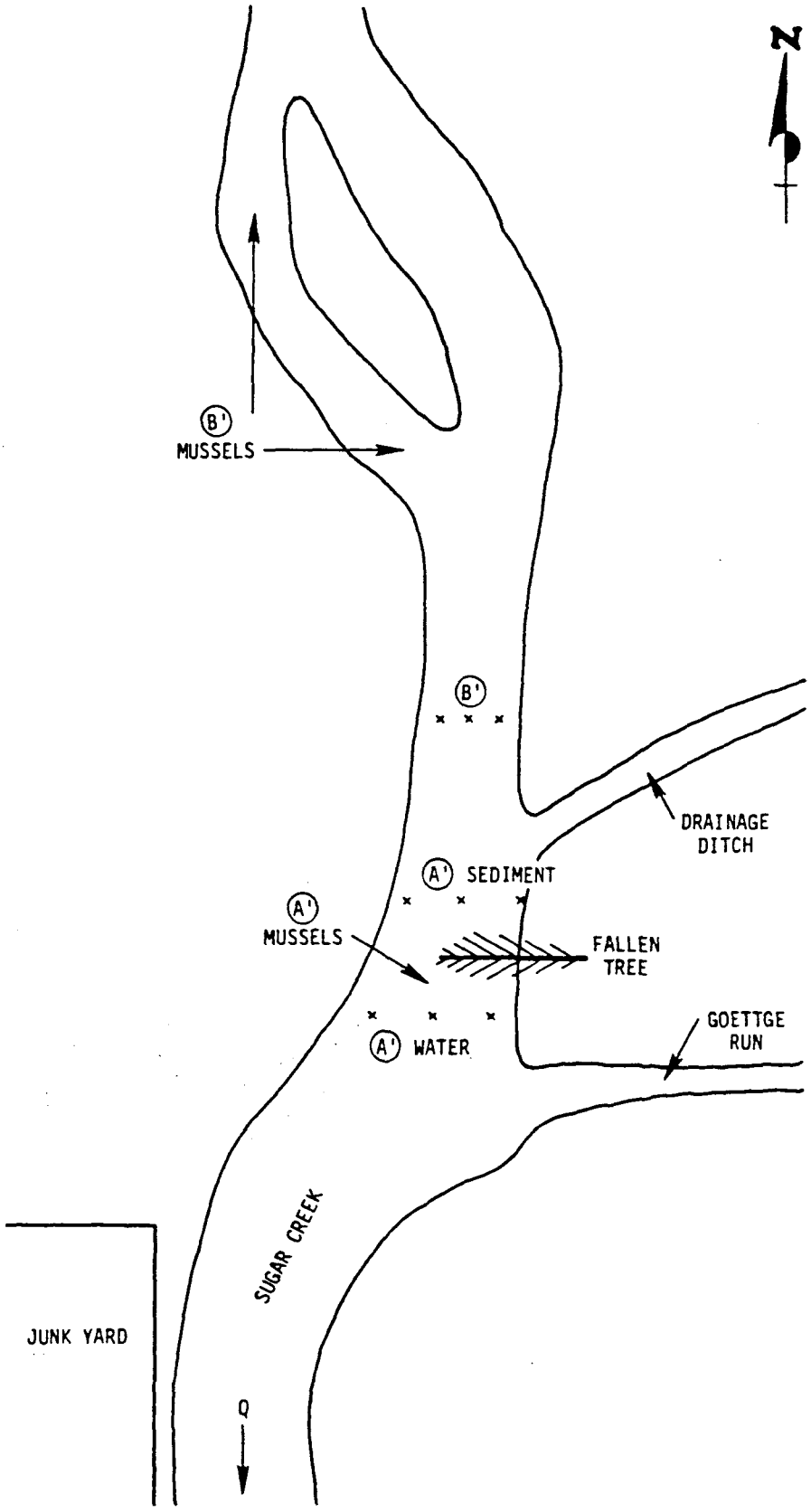



FIGURE 4.2 Location of sample points at Stations A' and B'.

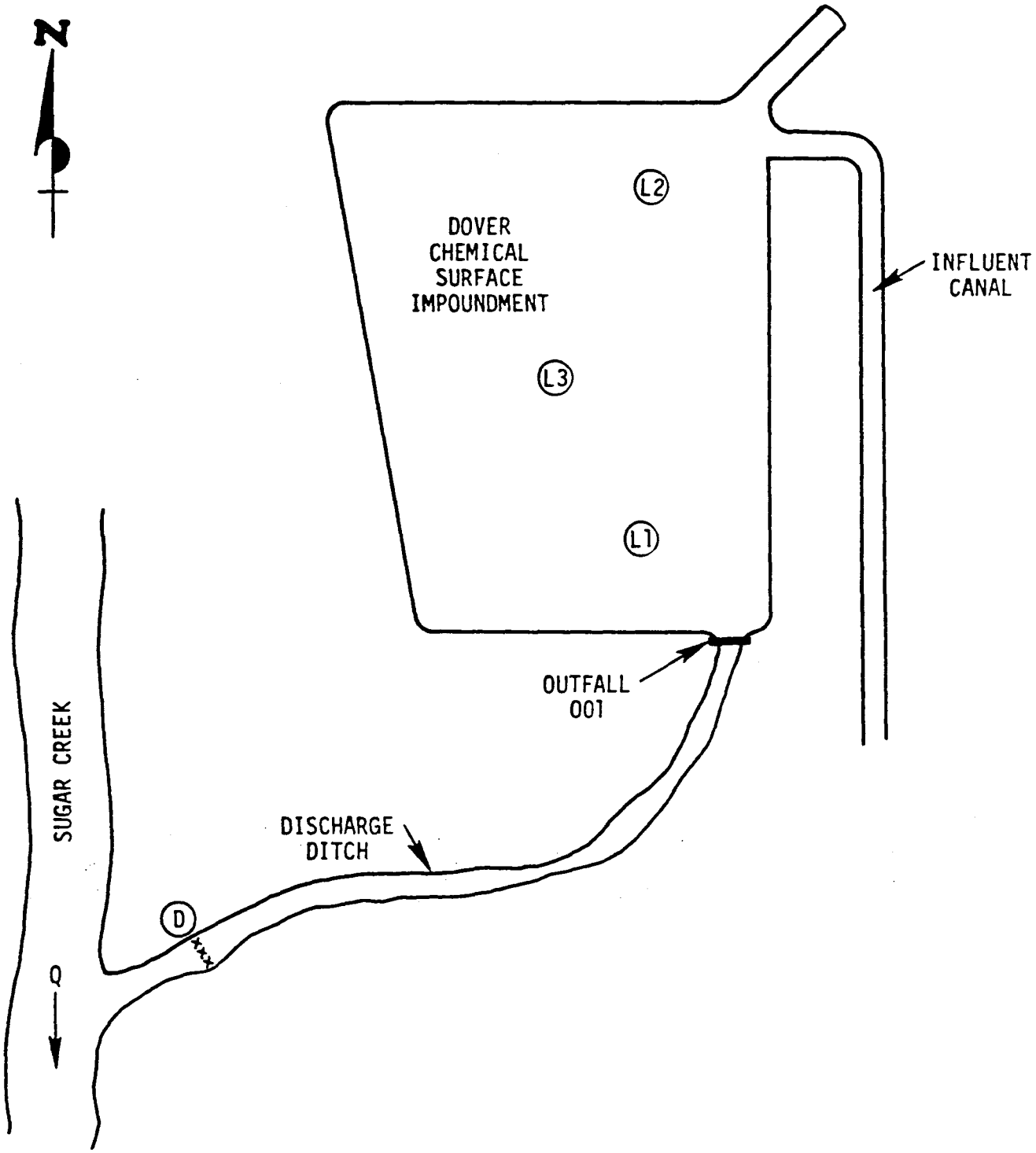



FIGURE 4.3

Location of sampling points in the Dover Chemical impoundment.

Table 1

SAMPLES TO BE COLLECTED

PLANT DISCHARGE WATERWAY

| Station / Medium: | Set I L1 | Set I L2 | Set I L3 | Set I D | Set II L1 | Set II L2 | Set II L3 | Set II D | Set III L1 | Set III L2 | Set III L3 | Set III D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sediment | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Mussel | 1 | 1 | 1 | 1 | - | - | - | - | - | - | - | - |
| QC Water | 1* | - | - | - | | | | | | | | |

SUGAR CREEK

| Station / Medium: | Set I B | Set I B' | Set I A' | Set I K | Set II B | Set II B' | Set II A' | Set II K | Set III B | Set III B' | Set III A' | Set III K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sediment | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Mussels | 1 | 1 | 1 | 1 | - | - | - | - | - | - | - | - |
| QC Water | 1* | - | - | - | - | - | - | - | - | - | - | - |

*Composite water sample 4-times volume of field samples.

Table 2

POTENTIAL ANALYSES

PLANT DISCHARGE WATERWAY

| Stations / Medium: | Set I L1 | Set I L2 | Set I L3 | Set I D | Set II L1 | Set II L2 | Set II L3 | Set II D | Set III L1 | Set III L2 | Set III L3 | Set III D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Filtered Water | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Suspended Solids | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sediment | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Mussels | 1 | 1 | 1 | 1 | - | - | - | - | - | - | - | - |
| QC Water | 2 | - | - | - | 2 | - | - | - | - | - | - | - |
| QC Filtrate | 2 | - | - | - | 2 | - | - | - | - | - | - | - |

SUGAR CREEK

| Stations / Medium: | Set I B | Set I B' | Set I A' | Set I K | Set II B | Set II B' | Set II A' | Set II K | Set III B | Set III B' | Set III A' | Set III K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Filtrated Water | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Suspended Solids | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sediment | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Mussels | 1 | 1 | 1 | 1 | - | - | - | - | - | - | - | - |
| QC Water | 2 | - | - | - | 2 | - | - | - | - | - | - | - |
| QC Filtrate | 2 | - | - | - | 2 | - | - | - | - | - | - | - |

Table 3

TOTAL SAMPLES BY SETS
(Plant Waterway and Sugar Creek Combined)

| Medium | Set I | Set II | Set III | All Sets |
|---|---|---|---|---|
| Water | 8 | 8 | 8 | 24 |
| Sediment | 8 | 8 | 8 | 24 |
| Mussels | 7 | 0 | 0 | 7 |
| QC Water | 2 | 0 | 0 | 2 |
| All Samples | 25 | 16 | 16 | 57 |

Table 4

TOTAL ANALYSES BY SETS
(Plant Waterway and Sugar Creek Combined)

| Medium | Set I | Set II | Set III | All Sets |
|---|---|---|---|---|
| Water (filtrate) | 8 | 8 | 8 | 24 |
| Suspended solids | 8 | 8 | 8 | 24 |
| Sediment | 8 | 8 | 8 | 24 |
| Mussels | 7 | 0 | 0 | 7(+7) |
| QC Water (filtrate) | 4 | 4 | 0 | 8 |
| QC Suspended solids | 4 | 4 | 0 | 8 |
| Potential Analyses | 39 | 32 | 24 | 95 |

To enhance study efficiency and minimize analytical costs, analyses will be conducted in a logical sequence of sets and possibly subsets. Three (3) sets are to be constructed such that the first set (set I) consists of the first samples of each type of medium collected at each of the eight stations. The second set (set II) comprises the second samples of each medium, etc. Subsets comprise all samples of a given medium within a set.

Samples will be analyzed sequentially by sets and by subsets within sets (see table 5). Analytical data from Set I will be evaluated to determine the need for analysis of Set II. Similarly, a decision to analyze set III would depend on the combined outcomes of set I and II.

The order of analyses of subsets within sets will be decided by MRI. Priority will be given to the analysis of samples collected from stations B, B', A', D, and K. Decisions on whether to continue analyses will be made at various points during the analytical process.

Within subsets, the extracted field samples and their respective QC blanks and spikes should be quantified in random order "blind" to the GC/MS operator.

4.1 Parameter Coverage

In addition to CP determinations, Temperature (C°), Flow (cfs), and Depth (feet) will be recorded for each sample.

4.2 Sample Collection

All samples will be collected and handled using procedures fully approved by EPA. A replicate set of samples will be provided to Dover Chemical Corp. for their independent analysis.

4.3 Sampling Preparations

All water column and sediment samples will be collected in glassware which has undergone the following cleaning steps:

- Remove surface residuals.
- Hot soapy soak to loosen and flotate most of residue.
- Hot water rinse to flush away flotated residue.
- Soak with deep penetrant or oxidizing agent to destroy traces of organic residue.
- Hot water rinse to flush away materials loosened by deep penetrant soak.

TABLE 5

PROPOSED SEQUENCE OF ANALYTICAL RUNS*
BY SETS AND SUBSETS

| | Run No. | Subset | |
|---|---|---|---|
| Set I | 1. | Filtered water | 8 field samples + 4 QA field samples** |
| | 2. | Suspended Solids | 8 field samples + 4 QA field samples** |
| | 3. | Sediment | 8 field samples |
| | 4. | Mussels | 7 field samples |
| Set II | 5. | Filtered water | 8 field samples + 4 QA field samples** |
| | 6. | Suspended Solids | 8 field samples + 4 QA field samples** |
| | 7. | Sediment | 8 field samples |
| | 8. | Mussels | 7 field samples (assuming mussels available) |
| Set III | 9. | Filtered water | 8 field samples |
| | 10. | Suspended Solids | 8 field samples |
| | 11. | Sediment | 8 field samples |
| | 12. | Mussels | NA |

* Analyses within each run are to be made in random sequence which is unknown (blind) to the operator.

** QA field samples collected from stations B and L1.

Method blanks will be analyzed with each run

- Rinse with deionized water to remove metallic deposits from the tap water.
- Rinse with high purity methanol followed by the high purity methylene chloride.

Glassware will be handled using polythene gloves to avoid contact with hands.

## 4.4 Water Column

All water column samples collected at stations A',B,B' and K will be a composite of single grab samples collected from at least three equidistant points along a stream transect. Each 0.5 gallon glass jar will be triple rinsed with stream water at the location the sample is to be collected. The jar will then be submerged in the stream until all air is replaced by a water sample. The water sample depth will be half way between the surface and the bottom of the stream. The samples collected along the stream transect will be composited to form a single sample.

Water samples collected at station D will be collected as a single grab in 0.5 gallon glass jars.

Water samples collected at stations L1, L2 and L3 will be depth integrated with discrete samples collected from three depths per station: near the bottom, at mid-depth and near the surface.

Field QA water samples will be collected as described in section 7.7.

All jars will be capped with teflon-lined lids. Water samples will require no preservative.

Each sample jar will be labeled with a barcode label.

## 4.5 Sediment Samples

All sediment samples will be collected in 500 ml. glass jars. At stations A', B, B' and K a stainless steel scoop will be used to remove sediment from the same equidistant points along the stream transect that the water column samples were collected. These discrete samples will then be composited to form a single sample.

At station D a stainless steel scoop will be used to remove sediment from that sample location.

At stations L1, L2 and L3 sediment samples will be collected using an Ekman dredge sampler.

Large rocks will be removed before placing the sample in the jars. All jars will be capped with teflon-lined lids. Sediment samples will require no preservation. Each sample jar will be labeled with the same information as described above. The stainless steel scoop and the Ekman dredge sampler will be triple rinsed with distilled water prior to filling a sample collection jar.

## 4.6 Tissue Samples

Mussel samples will be collected from the Sugar Creek stations in one of two manners, depending upon the depth of the stream. Generally, where the stream is 6 inches or less in depth, the mussels will be collected by hand. In areas where water depth exceeds 6 inches, a clam rake will be utilized to collect samples as visual observations will not be possible. If mussels cannot be found at a given Sugar Creek station after 2 hours of sampling, mussel sampling will be aborted at that station.

Mussels are not expected to habitate the lagoon or the drainage ditch. However, if there is evidence that mussels exist in the lagoon, sampling of mussels will be conducted only if, after 15 minutes of sampling, a sufficient number of specimens are collected to warrant further investigation.

Unhealthy or dead mussels will be discarded. All live mussels will be placed on ice in coolers.

In accordance with the permit obtained for the Sugar Creek area from the Ohio Department of Natural Resources, no more than 10 mussel specimens will be collected from each of the stations deployed in the receiving water proper. Also, following shipment to the lab, the shells will be removed from the specimens collected from the field and shipped back to the State of Ohio thus fulfilling the requirements of the permit.

## 4.7 Sample Preservation And Transportation

All sample jars will be kept in coolers out of direct sunlight

and transported in ice-filled coolers with sufficient packaging material to reduce the possibility of breakage. Any live mussels collected during the study will also be placed in an ice-filled cooler. This is expected to keep the mussels alive while being transported to the MRI Laboratory in Kansas City. All water, sediment, and mussel samples will be shipped via commercial airlines or by overnight delivery service, to MRI's Kansas City Laboratory.

Upon arrival at the MRI laboratory, the samples will be logged in and separated into sets as described above. The first set to be analyzed, will be extracted within the first seven (7) days from date of collection. The remaining samples will be refrigerated until extraction. All samples will be analyzed within thirty (30) days from date of collection.

## 5.0 References

1. 1986 State Section 305(b) report for the State of Ohio - draft.

2. PEI Associates, Inc. 1984, Exposure Assessment of Chlorinated Paraffins, Washington, DC

# APPENDIX B

## FIELD STUDY DESIGN AND SAMPLING PROTOCOL

## FOR

## TINKERS CREEK

## BEDFORD, OHIO

# APPENDIX B - TABLE OF CONTENTS


| Section | Heading | Revision | Date |
|---|---|---|---|
| 1.0 | Description of the Study Area | | 10/14/86 |
| 2.0 | Waste Inputs | | 10/14/86 |
| 2.1 | Description of the CP cutting oil user | | 10/14/86 |
| 3.0 | Reconnaissance Survey | | 10/14/86 |
| 4.0 | Field Study Design | | 10/14/86 |

## 1.0 Description of the Study Area

Tinkers Creek is located in Northeast Ohio. From its source it flows south and then to Northeast toward its confluence with the Cuyahoga River.

The drainage basin of Tinkers Creek is largely industrialized and urban. The focus of this field study is on the upper reaches of Tinkers Creek and tributaries in the Walton Hills area. A map/schematic of this segment of Tinkers Creek is given in Figure 1.1.

The tributaries to Tinkers Creek in the study area are small surface streams 3 to 5 ft wide and several inches deep at the point where they flow under Egbert Road. These streams have gravel and silt bottoms and are easily accessed at this point. Deerlick Run, at the point of its confluence with Tinkers Creek is 8 to 10 feet wide, 6 inches deep and has a shale bedrock and coarse gravel bottom. Tinkers Creek, at it confluence with its tributary Deerlick Run, is about 50 feet wide, 1 to 3 feet deep and has a coarse gravel and shale bedrock bottom. Deerlick Run and Tinkers Creek have relatively steep gradients; several waterfalls and rapids are present in this area. Flow is estimated at 100 - 150 cfs. (During the spring, Tinkers Creek has Class V whitewater.) During summer low flow conditions about 80 percent of the volume of Tinkers Creek is contributed by upstream sewage effluents. The Ohio EPA (OEPA) reported that no mussels would be found in any of these streams.

Several oil spills and industrial releases have impacted these tributaries in recent years. OEPA previously has conducted monitoring and toxicity studies on these streams. Their studies indicate the presence of stream pollution from many sources in this area, termed the Deerlick Run Drainage Network.

## 2.0 Waste Inputs

In the study area, there are at least 17 industrial facilities (e.g, chemical manufacturers, metal fabricators, concrete plants, drum recyclers, etc.) and two hazardous waste sites (S. K. Wellman's electroplating sludge pond which is currently being closed and American Steel Drum Recyclers which was previously cleaned-up by EPA) located in the close proximity to each other. (Figure 2-1) Many of these facilities have nonpoint discharges to the same tributaries to Tinkers Creeks that are influenced by the point source discharger in the area that is a supposed CP lube oil user.

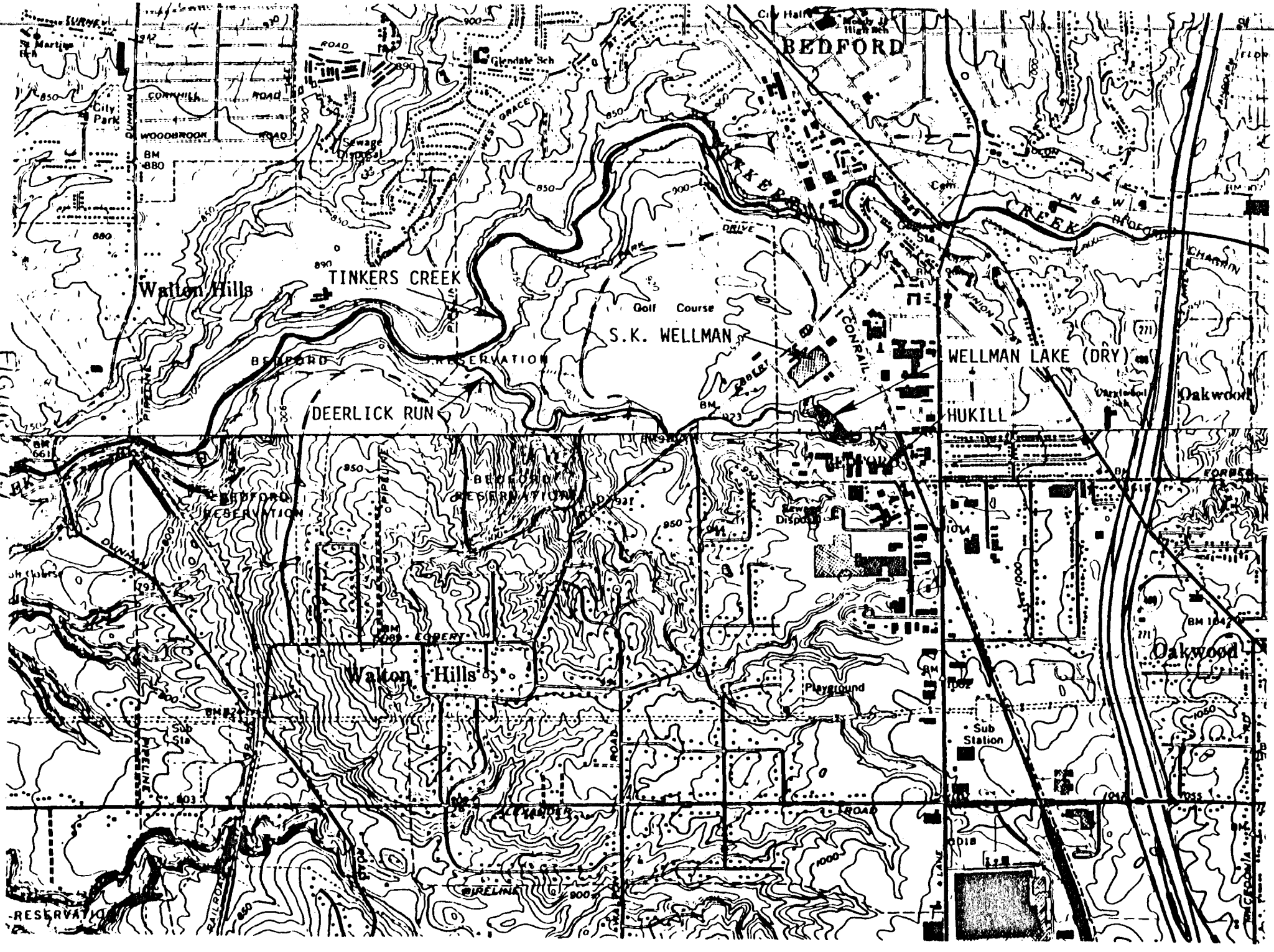
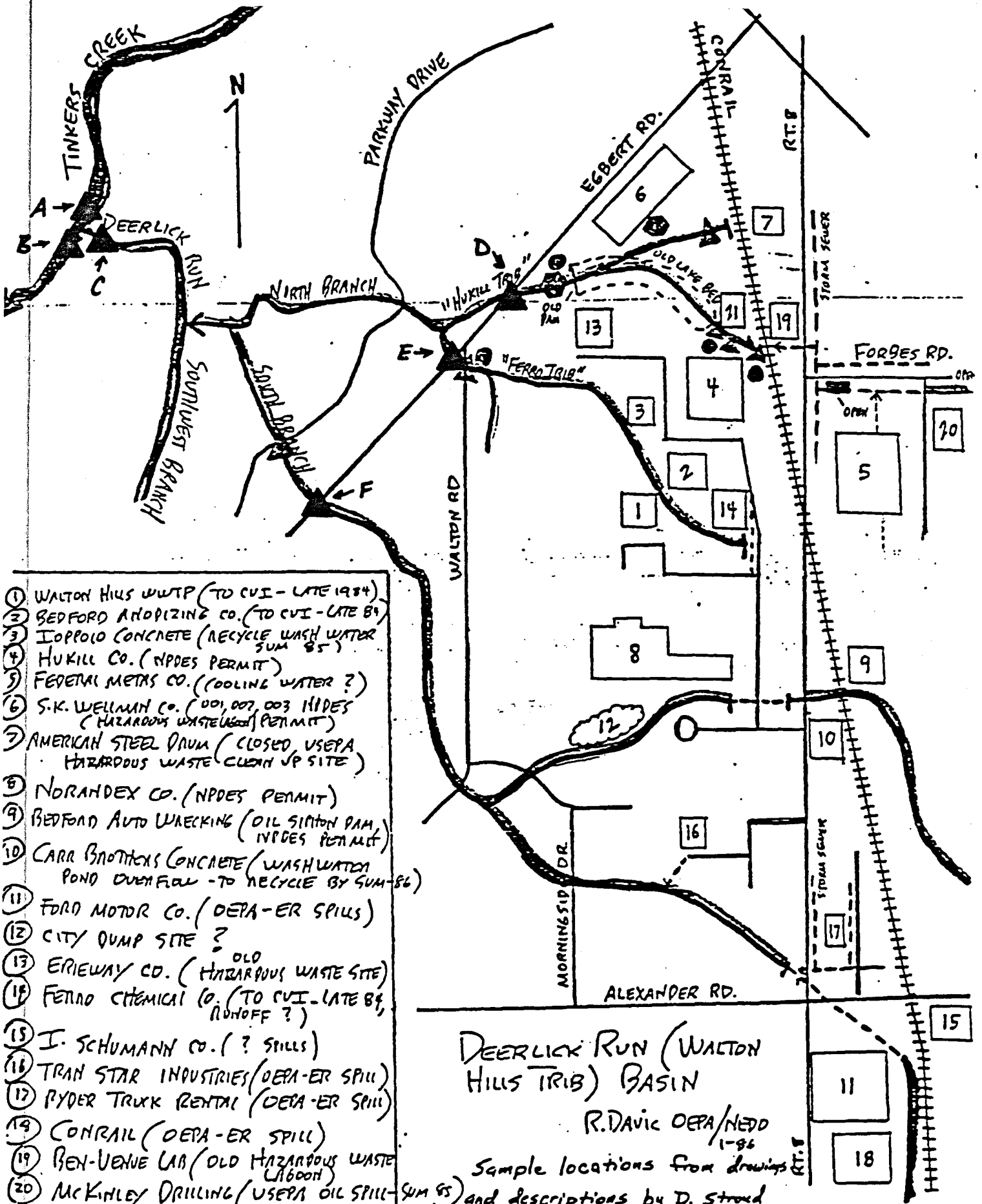

BEDFORD
City Hall
Glendale Sch
City Park
Sewage Disposal
Walton Hills
TINKERS CREEK
Golf Course
S.K. WELLMAN
WELLMAN LAKE (DRY)
BEDFORD RESERVATION
DEERLICK RUN
HUKILL
Oakwood
Walton Hills
Playground
Sub Station
Sub Sta
N & W
CONRAIL
RESERVATION

FIGURE 1




1. WALTON HILLS WWTP (TO CVI - LATE 1984)
2. BEDFORD ANODIZING CO. (TO CVI - LATE 84)
3. IOPPOLO CONCRETE (RECYCLE WASH WATER SUM 85)
4. HUKILL CO. (NPDES PERMIT)
5. FEDERAL METALS CO. (COOLING WATER ?)
6. S.K. WELLMAN CO. (001, 007, 003 NPDES PERMIT) (HAZARDOUS WASTE LAGOON)
7. AMERICAN STEEL DRUM (CLOSED, USEPA HAZARDOUS WASTE CLEAN UP SITE)
8. NORANDEX CO. (NPDES PERMIT)
9. BEDFORD AUTO WRECKING (OIL SIPHON DAM, NPDES PERMIT)
10. CARR BROTHERS CONCRETE (WASH WATER POND OVERFLOW - TO RECYCLE BY SUM-86)
11. FORD MOTOR CO. (OEPA-ER SPILLS)
12. CITY DUMP SITE ?
13. EPRIEWAY CO. (OLD HAZARDOUS WASTE SITE)
14. FERRO CHEMICAL CO. (TO CVI - LATE 84, RUNOFF ?)
15. I. SCHUMANN CO. (? SPILLS)
16. TRAN STAR INDUSTRIES (OEPA-ER SPILL)
17. RYDER TRUCK RENTAL (OEPA-ER SPILL)
18. CONRAIL (OEPA-ER SPILL)
19. BEN-VENUE LAB (OLD HAZARDOUS WASTE LAGOON)
20. McKINLEY DRILLING (USEPA OIL SPILL - SUM 85)
21. S.K. WELLMAN (HAZARDOUS WASTE LAGOON)

● 1981-82 Sample Sites ▲ 1985 Sample Sites

1984 Grab Sites

DEERLICK RUN (WALTON HILLS TRIB) BASIN

R. DAVIC OEPA/NEDO 1-86

Sample locations from drawings & and descriptions by D. Stroud and K. Rogers OEPA/NEDO, 3/2/82, 1984, 3/26/85. Composite of drawings by E. Nygaard 8/19/86.

FIGURE 2-1

## 2.1 The CP User

A metal-working industry located in the study area is a supposed user of cutting oils containing chlorinated paraffins as an additive.

This Company operates a plant that manufactures clutch and brake friction materials for trucks and heavy equipment. While OEPA officials could not confirm that CPs are used in the process, other sources of information indicate that these oils are used. Process wastewaters discharge to the city of Bedford's POTW. Pollutants including heavy metals (mainly copper), ammonia, oil, grease, and acids and bases are present in the process wastewater. Noncontact cooling water and storm water are discharged from the plant property through NPDES outfalls to a discrete conveyance (i.e., a small surface stream) that flows a distance of about 2 km before it enters Tinkers Creek. It is likely that ground water carrying contaminants from past waste management practices (i.e., surface impoundments) located on-site also enters this tributary to Tinkers Creek. This company employs about 250 employees.

The tributaries impacted by this plant and the other point source dischargers originate immediately upgradient of these sites. Storm sewer outfalls, runoff, ground water and nonpoint source discharges are the sources of flow. There are no non-impacted upstream control sites. Tinkers Creek is impacted by POTW and industrial outfalls upstream of its confluence with Deerlick Run.

## 3.0 Reconnaissance Survey

On October 1 and 2, 1986, a site reconnaissance was conducted in the study area by Tom Janszen and Bob Hoye of PEI. Additionally, a meeting was held with Ohio EPA representatives on October 2 to discuss their knowledge of the operations conducted at this facility, the physical setting of this and other plants in the area and their discharges to surface waters. The purpose of the visit was to gather the information necessary to make a decision regarding sampling of surface waters, sediments and mussels for CP analysis.

The PEI representatives were able to meet with the Ohio EPA but were able to obtain only limited information about the proposed sampling area. They obtained one toxicity evaluation report for the area which is available under separate cover.

The PEI representatives were also able to visit the proposed site, photograph prospective sampling sites, and evaluate the hydrology of the area.

Their efforts produced the following information about the area.

- There is no indication of mussels or any oter macro-invertebrates or fish in the proposed study area. In the best judgement of the Reconnaissance Team, it is unlikely that mussels will be found in the area.

- Because Tinkers Creek flows through the Cleveland Metroparks Bedford Reservation in the proposed study area, permission to take samples from Tinkers Creek and Deerlick Run must be obtained from the Metroparks Administration.

- No special sampling gear will be required if the field study is implemented.

- Streams in the study area are generally accessible especially at the sample locations desicribed later in this Appendix.

- Stream samples collected in this area will likely contain a variety of organic and metal constituents from past and current operations in the area.

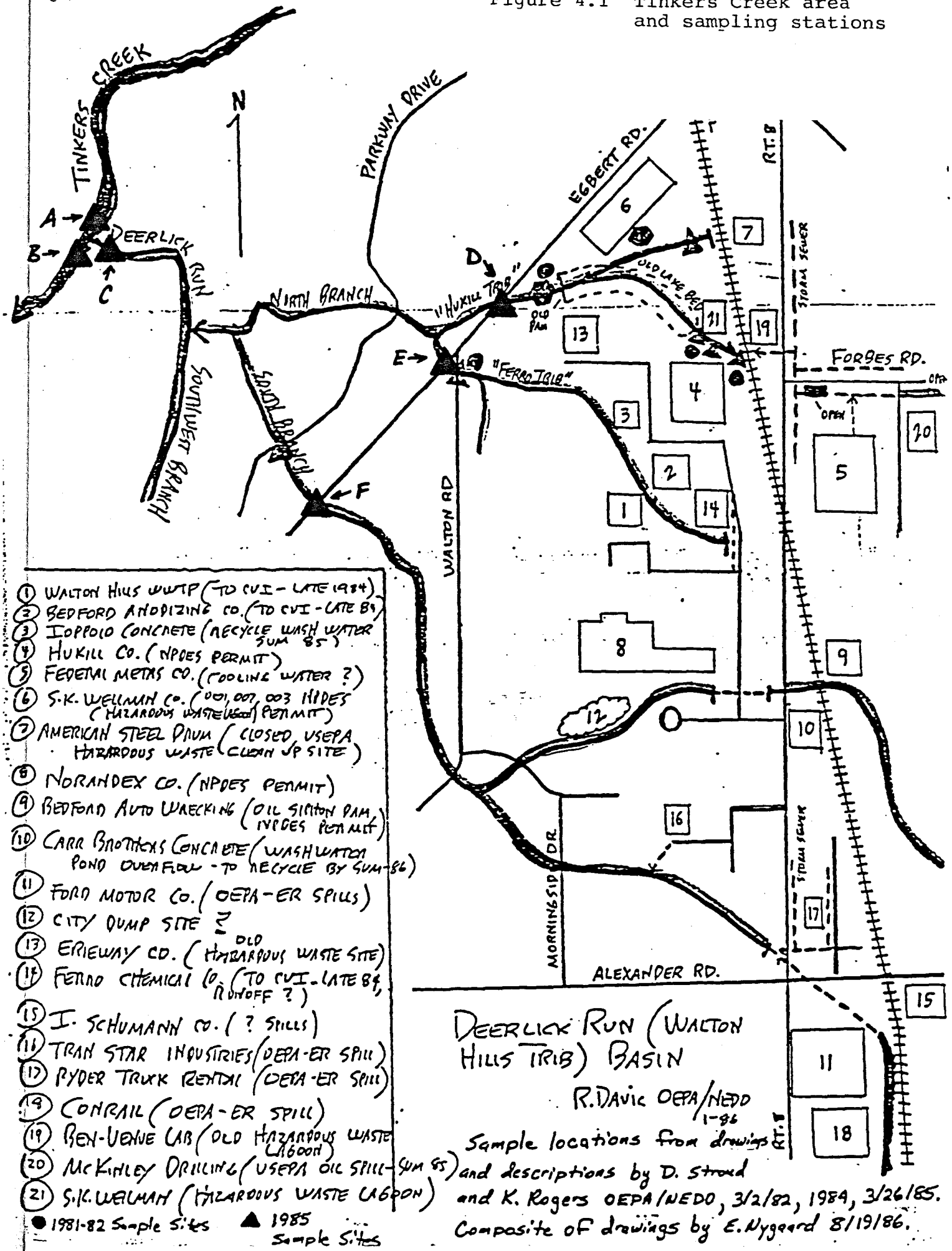
- Sediment samples will be limited to gravel and rock although some silt may be obtainable from the upstream tributaries to Deerlick Run.

## 4.0 Field Study Design

The design for this study has necessarily been developed without the knowledge of the frequency of occurrence of residues in the study area(s) or the statistical parameters of such residues. The design has also been developed with the expectation that the precision and accuracy of the analytical method (which is concurrently being determined) will be acceptable.

The design calls for a total of 6 samplings stations; 2 stations in Tinkers Creek, one on Deerlick Run at its confluence with Tinkers Creek, and one each on Hukill Tributary, Ferro Tributary and South Branch at Egbert Road. The station locations are shown in Figures 4.1, 4.2 and 4.3. A seventh sample station will be established to capture a sample of the process wastestream (or wastewater sludge if a wastestream sample cannot be collected) from the plant effluent of the supposed CP cutting oil user.

Figure 4.1 Tinkers Creek area and sampling stations




1. WALTON HILLS WWTP (TO CVI - LATE 1984)
2. BEDFORD ANODIZING CO. (TO CVI - LATE 84)
3. IOPPOLO CONCRETE (RECYCLE WASH WATER SUM 85)
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18. CONRAIL (OEPA-ER SPILL)
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20. McKINLEY DRILLING (USEPA OIL SPILL - SUM 85)
21. S.K. WELLMAN (HAZARDOUS WASTE LAGOON)

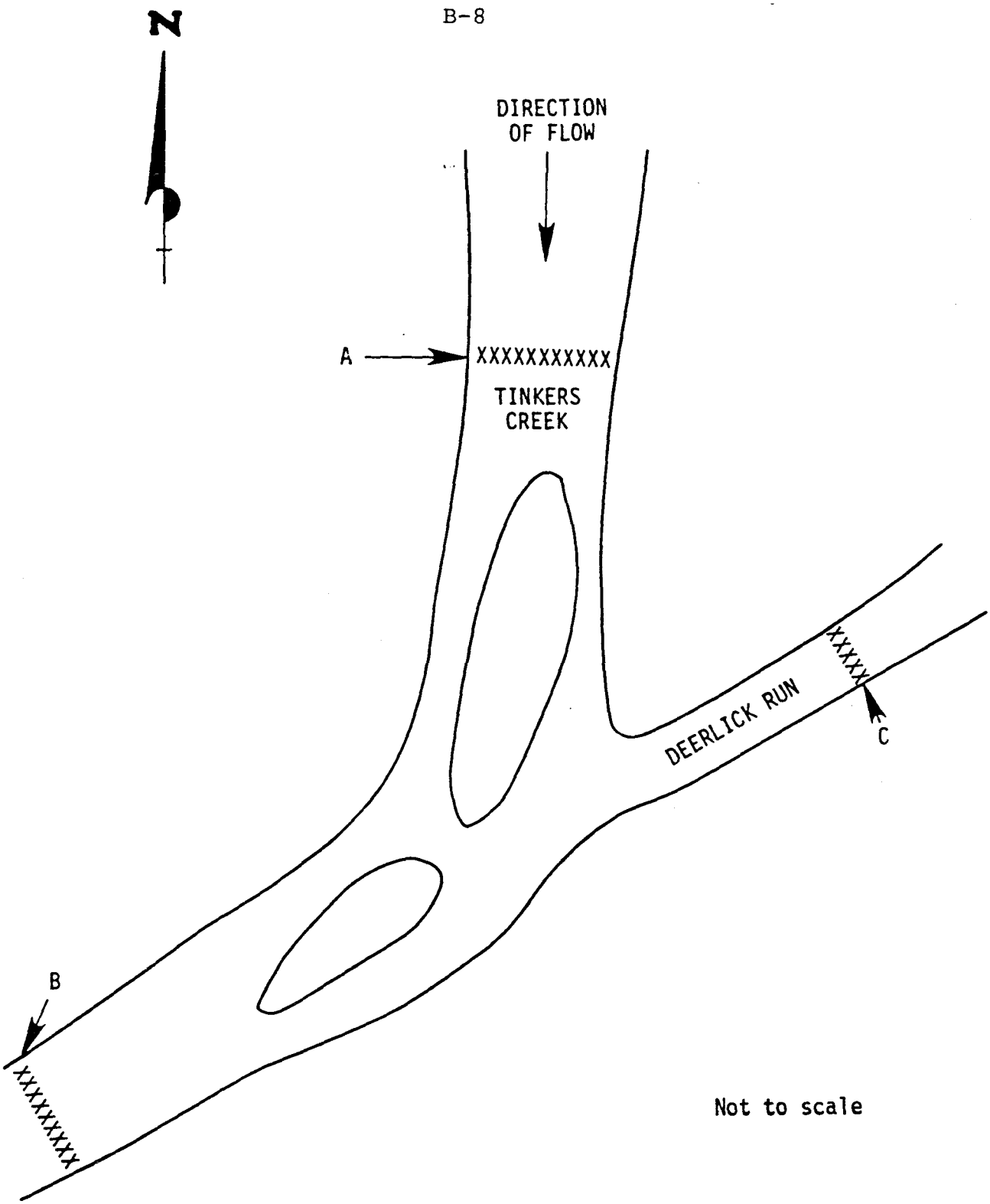


Figure 4.2 Location of Sampling Stations A through C at the confluence of Tinker's Creek and Deerlick Run.

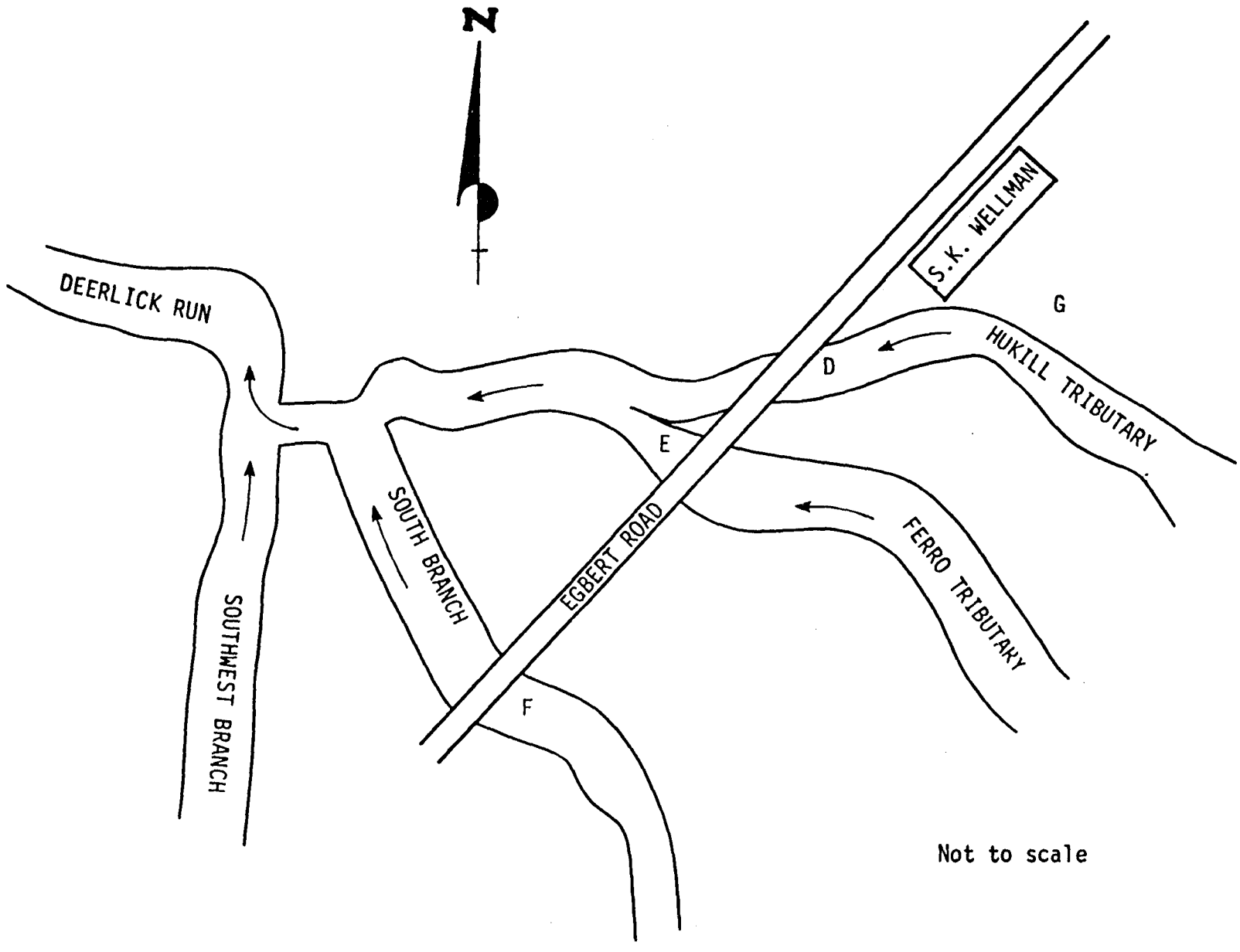


Figure 4.3 Location of Sampling Stations D through G.

| Station ID | Location |
|---|---|
| A | Tinkers Creek immediately upstream of Deerlick Run Confluence |
| B | Tinkers Creek immediately downstream from Deerlick Run confluence |
| C | Deerlick Run at its confluence with Tinkers Creek |
| D | Hukill Tributary downstream from Wellman discharge and at Egbert Road |
| E | Ferro Tributary at Egbert Road |
| F | South Branch at Egbert Road. |
| G | A representative site to capture the process wastestream (or sludge). |

The design requires the collection of a minimum of three individual grab or composite water and sediment samples at each of the stations. The samples and analyses comprising each set are shown in Tables 1 through 4.

To enhance study efficiency and minimize analytical costs, analyses will be conducted in a logical sequence of sets and possibly subsets. Three (3) sets are to be constructed such that the first set (set I) consists of the first samples of each type of medium collected at each of the stations. The second set (set II) comprises the second samples of each medium, etc.

Samples will be analyzed sequentially by sets and by subsets within sets (see table 5). Analytical data from Set I will be evaluated to determine the need for analysis of Set II. Similarly, a decision to analyze set III would depend on the combined outcomes of sets I and II.

The order of analyses of subsets within sets will be decided by MRI. Decisions on whether to continue analyses will be made at various points during the analytical process.

Within subsets, the extracted field samples and their respective QC blanks and spikes should be quantified in random order "blind" to the GC/MS operator.

Table 1

SAMPLES TO BE COLLECTED

TINKERS CREEK AND TRIBUTARIES

| Station Medium: | Set I A | B | C | D | E | F | G* | Set II A | B | C | D | E | F | G* | Set III A | B | C | D | E | F | G* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sediment | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | - |
| Tissue** | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | - |
| QC Water*** | 1 | - | - | 1 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |

* If accessible

** Subject to availability

*** Composite water sample 4 times volume of field samples

Table 2

TOTAL SAMPLES BY SETS

| Medium | Set I | Set II | Set III | All Sets |
|---|---|---|---|---|
| Water | 6 | 6 | 6 | 18* |
| Sediment | 6 | 6 | 6 | 18 |
| Tissue | 6 | 0 | 0 | 6 |
| QC Water | 2 | 0 | 0 | 2 |
| All samples | 20 | 12 | 12 | 44* |

* An additional three (3) samples may be added if a process wastewater sample can be obtained

Table 3

POTENTIAL ANALYSES

TINKERS CREEK AND TRIBUTARIES

| Stations | Set I | | | | | | | Set II | | | | | | | Set III | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Medium: | A | B | C | D | E | F | G | A | B | C | D | E | F | G | A | B | C | D | E | F | G |
| Filtrate | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| TSS | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sediment | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | - | 1 | 1 | 1 | 1 | 1 | 1 | - |
| Tissue | 1 | 1 | 1 | 1 | 1 | 1 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| QC Water | 2 | - | - | 2 | - | - | - | 2 | - | - | 2 | - | - | - | - | - | - | - | - | - | - |
| QC filter | 2 | - | - | 2 | - | - | - | 2 | - | - | 2 | - | - | - | - | - | - | - | - | - | - |

Table 4

TOTAL ANALYSES BY SETS

TINKERS CREEK AND TRIBUTARIES

| Medium | Set I | Set II | Set III | All Sets |
|---|---|---|---|---|
| Water (filtrate) | 6 | 6 | 6 | 18* |
| TSS | 6 | 6 | 6 | 18* |
| Sediment | 6 | 6 | 6 | 18 |
| Tissue | 6 | 0 | 0 | 6 |
| QC water (filtrate) | 4 | 4 | 0 | 8 |
| QC water (TSS) | 4 | 4 | 0 | 8 |
| Potential Analyses | 32 | 26 | 18 | 74 |

* If a process wastewater sample can be obtained, this number will increase by three (3).

Table 5

PROPOSED SEQUENCE OF ANALYTICAL RUNS*
BY SETS AND SUBSETS

| | Run No. | Subset | | |
|---|---|---|---|---|
| Set I | 1 | Filtered water | 6 field samples | + 4 QC field samples ** |
| | 2 | TSS | 6 field samples | + 4 QC field samples ** |
| | 3 | Sediment | 6 field samples | |
| | 4 | Tissue | 6 field samples | (subject to availability) |
| Set II | 5 | Filtered water | 6 field samples | + 4 QC field samples ** |
| | 6 | TSS | 6 field samples | + 4 QC field samples ** |
| | 7 | Sediment | 6 field samples | |
| | 8 | Tissue | 6 field samples | (subject to availability) |
| Set III | 9 | Filtered water | 6 field samples | |
| | 10 | TSS | 6 field samples | |
| | 11 | Sediment | 6 field samples | |
| | 12 | Tissue | 6 field samples | (subject to availability) |

* Analyses within each run are to be made in random sequence which is unknown (blind) to the operator.

** QA field samples collected from stations A and D
Method blanks will be analyzed with each run

## 4.1 Parameter Coverage

In addition to CP determinations, Temperature (C°), Flow (cfs), and Depth (feet) will be recorded for each sample.

## 4.2 Sample Collection

All samples will be collected and handled using procedures fully approved by EPA.

## 4.3 Sampling Preparations

All water column and sediment samples will be collected in glassware which has undergone the following cleaning steps:

- Remove surface residuals.
- Hot soapy soak to loosen and flotate most of residue.
- Hot water rinse to flush away flotated residue.
- Soak with deep penetrant or oxidizing agent to destroy traces of organic residue.
- Hot water rinse to flush away materials loosened by deep penetrant soak.
- Rinse with deionized water to remove metallic deposits from the tap water.
- Rinse with high purity methanol followed by the high purity methylene chloride.

Glassware will be handled using polythene gloves to avoid contact with hands.

## 4.4 Water Column

All water column samples collected at stations A, B & C will be a composite of single grab samples collected from at least three, but if possible five or more equidistant points along a stream transect. Each 0.5 gallon glass jar will be triple rinsed with stream water at the location the sample is to be collected. The jar will then be submerged in the stream until all air is replaced by a water sample. The water sample depth will be half way between the surface and the bottom of the stream. The samples collected along the stream transect will be composited to form a single sample.

Water samples collected at station D, E, F and G will be collected as a single grab in 0.5 gallon glass jars. These should be collected near midstream.

Field QA water samples will be collected as described in Section 7.7.

All jars will be capped with teflon-lined lids. Water samples will require no preservative.

Each sample jar will be labeled with a barcode label.

If, in the judgement of the field crew, more water should be collected in order to facilitate a more successful total suspended solids analysis, additional samples should then be collected. Conversely, if, in the judgement of the field crew, additional sample collection will lend little towards this end, then no additional water samples should be collected.

## 4.5 Sediment Samples

All sediment samples will be collected in 500 ml. glass jars. At stations A, B and C a stainless steel scoop and/or Ekman dredge will be used to remove sediment from the same equidistant points along the stream transect that the water column samples were collected. These discrete samples will then be composited to form a single sample. If sediment is not available at these points, the most representative sample possible will be obtained from these sites and the precise location will be documented.

At stations D, E and F a stainless steel scoop and/or Ekman dredge will be used to collect sediment.

## 4.6 Tissue Samples

Attempts will be made to collect biological organisms from the stream bottom at stations A, B, C, D, E and F. Sediment scoops will be seived using a U.S. Standard No. 30 Sieve and invertebrate larval forms (esp., chironomid larvae) will be collected for analysis, if available. If dredging and sieving is not appropriate given the nature of the stream, then collections should be made manually by overturning rocks and rubble. If sufficient biological organisms cannot be found over 2 hours of sampling at any given station further biological collection will be abandoned.

## 4.7 Sample Preservation And Transportation

All sample jars will be kept in coolers out of direct sunlight and transported in ice-filled coolers with sufficient packaging material to reduce the possibility of breakage. All water, sediment, and tissue samples will be shipped via commercial airlines or by overnight delivery services, to MRI's Kansas City Laboratory.

Upon arrival at the MRI laboratory, the samples will be logged in and separated into sets as described above. The first set analyzed, will be extracted within the first seven (7) days from date of collection. The remaining samples will be refrigerated until extraction. All samples will be analyzed within thirty (30) days from date of collection.

# APPENDIX C

# ANALYTICAL METHOD

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## 1. SCOPE AND APPLICATION

This method provides procedures for the detection and semiquantitative measurement of chlorinated paraffins in water, suspended solids, sediment and mussel tissue. Chlorinated paraffins measured with this method are C10-C12, 50-60%, Cl; C14-C17, 50-60%; and C20-C30, 40-50% Cl.

## 2. SUMMARY OF METHOD

Figure 1 presents a schematic of the analytical procedures for determining chlorinated paraffins in water, sediment, suspended solids, and mussel tisse. The method requires sample preparation, extraction of chlorinated paraffins, cleanup, concentration, and determination by high resolution gas chromatography/negative chemical ionization mass spectrometry/selected ion monitoring (HRGC/NCIMS/SIM).

## 3. DEFINITIONS

### 3.1 Concentration Calibration Solution

Solutions containing known amounts of analytes. These calibration solutions are used to determine instrument response of the analytes as a function of mass.

### 3.2 Sample Batch

A sample batch consists of up to 10 environmental samples of the same matrix, one laboratory method blank, and two internal quality control samples (one spiked and one unspiked). Additional QC samples (e.g., field QC samples, trip QC samples) may be added to a sample batch where appropriate.

### 3.3. Laboratory Method Blank

This blank is prepared in the laboratory through performing all analytical procedures except addition of a sample aliquot to the extraction vessel. A minimum of one laboratory method blank will be analyzed with each batch of samples.

### 3.4 Laboratory Method Spike

This sample consists of an aliquot of matrix to which an known amount of analyte is added. All analytical procedures are performed on this spike. A minimum of one laboratory spike is analyzed with each batch of samples, where appropriate, to monitor recovery for that batch.

### 3.5 Field QC Samples

A sample collected in the field, homogenized, and divided into four aliquots. Two of the aliquots are spiked in the field (field spikes) and two are left unspiked (field blanks). The

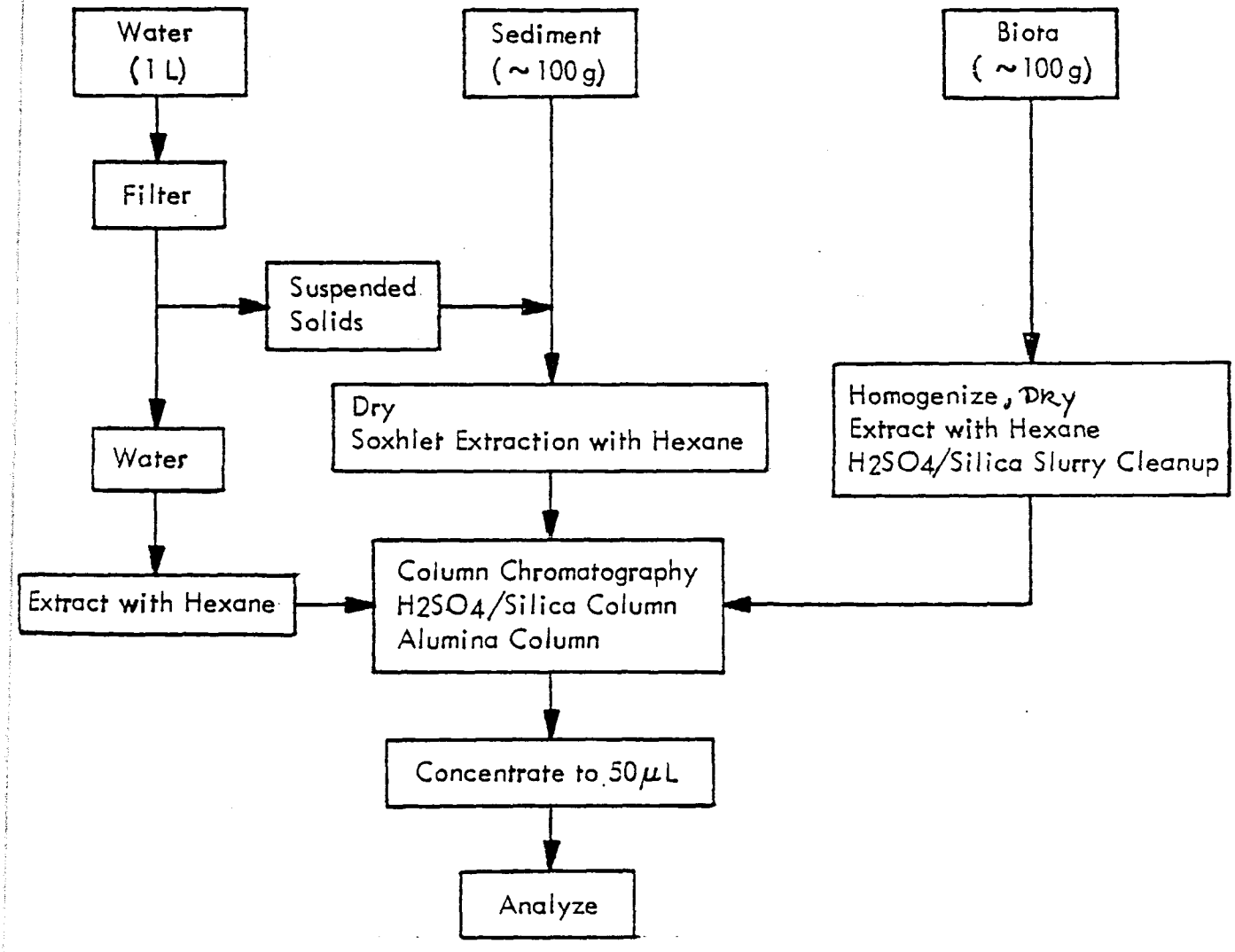


Figure 1 Proposed extraction and clean-up procedures for chlorinated paraffins.

field blanks are spiked in the laboratory at the same level as the field spikes, analyzed, and compared to the field spikes to monitor analyte behavior during transportation and storage.

3.6 Trip QC Samples

Blank matrix samples prepared in the laboratory, taken and maintained on the sampling trip. Half of the samples are spiked in the field and the remaining half left unspiked. The samples are transported, stored, and analyzed in the laboratory in the same manner as the environmental samples. These samples are used to monitor contamination of the environmental samples. For this method, deionized water served as the trip sample matrix.

3.7 Performance Sample

A standard solution of analytes prepared by the work assignment QCC at a concentration unknown to the analyst. This sample is analyzed by the analyst and the results reported to the QCC for evaluation. This sample is designed to measure instrument performance.

## 4. INTERFERENCES

Chemicals which elute from the HRGC column within the retention time windows of the chloroparaffins and produce ions within the mass ranges scanned are potential interferences. Because low levels (sub ppb) of chlorinated paraffins are anticipated, the elimination of the interferences is essential. High purity reagents and solvents must be used and all equipment must be throughly cleaned. Because chlorinated paraffins are used as plasticizers, contact with plastics (except polyethylene) must be avoided. Polyethylene gloves should be worn during sample preparation to avoid contamination of the samples. Laboratory method blanks must be analyzed to demonstrate the absence of contamination that would interfere with the measurement of the chlorinated paraffins. Column chromatographic procedures are used to remove co-extracted sample components; these procedures must be performed carefully to minimize loss of chlorinated paraffins during attempts to increase their concentration relative to other sample components.

## 5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. Chloroparaffins have been shown to be carcinogenic. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

5.2 All laboratory personnel will be required to wear laboratory coats or coveralls, polyethylene gloves, and safety glasses. The neat standards, stock, and working solutions will be handled only in a Class A fume hood or glove box. When manipulating stock standards or working solution, the analyst is advised to place the solution vials in a secure holder (sample block or glass beaker) to prevent accidental spills.

5.3 If stock or working standards are spilled, absorb as much as possible with absorbent paper and place in a container clearly labelled as chlorinated paraffin waste. Solvent wash all contaminates surfaces with acetone and absorbent paper.

5.4 If handling of these compounds results in skin contact, immediately remove all contaminated clothing and wash the affected skin areas with soap and water for at least 15 min.

5.5 Disposal of Laboratory Wastes

All laboratory wastes (solvents and absorbents) will be disposed of as hazardous wastes.

## 6. APPARATUS AND EQUIPMENT

6.1 High Resolution Gas Chromatograph/Negative Chemical Ionization Mass Spectrometer/Data System.

6.1.1 The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and a fused silica capillary column. The injector must be an on-column injector capable of allowing direct injection with a fused silica syringe. When using this method, a 1-µl injection volume is recommended. Since this method does not employ an internal standard, injection volumes for all extracts, blanks, and calibration solutions must be consistent.

6.1.2 High Resolution Gas Chromatograph-Mass Spectrometer Interface

It is recommended that the HRGC column be fitted directly into the MS ion source. If an interface is used, all components should be glass or glass-lined stainless steel. The interface components should be compatible with 300°C temperature, and should be appropriately designed so that the separation of the chlorinated paraffins which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and active surfaces (adsorption sites) in the interface may cause sample losses.

6.1.3 Mass Spectrometer

The mass spectrometer must be equipped with a negative chemical ionization source and associated hardware, and must be operated in the selected ion monitoring mode with a total cycle time of 3 s or less.

6.1.4 Data System

A dedicated hardware or data system is required to control the rapid selected ion monitoring process and to acquire the data. Quantitation data (peak areas) and SIM traces must be acquired during the analysis. Quantitations are reported based on computer generated peak areas.

6.2 HRGC Column

A 30-m x 0.25-mm ID fused silica capillary column coated with DB-5 (0.25 µm) is used for analysis of chloroparaffins.

6.3 Miscellaneous Equipment

6.3.1 Nitrogen evaporation apparatus with variable flow rate.

6.3.2 Balance capable of accurately weighing to 0.01 g.

6.3.3 Balance capable of accurately weighing to 0.0001 g.

6.3.4 Water bath equipped with concentric ring cover and capable of being temperature controlled.

6.3.5 Stainless steel spatulas or chemical spoons.

6.3.6 Magnetic stirrers and stir bars.

6.4 Glassware

6.4.1 Separatory Funnels, 2 L

6.4.2 Kuderna-Danish (KD) apparatus

6.4.3 Soxhlet apparatus

6.4.4 Erlenmeyer flasks

6.4.5 Minivials

2-mL borosilicate glass with conical-shaped reservoir and screw caps lined with teflon®-faced silicone disks.

6.4.6 Powder funnels - glass

6.4.7 Chromatographic columns for the silica and alumina chromatography - mini champagne columns wit 30 mL reservoirs (Supelco).

6.4.8 Carborundum boiling chips; extracted for 6 h in a soxhlet apparatus with benzene and air dried.

6.4.9 Glass Wool, silanized (Supelco); extracted with methylene chloride and hexane and air dried.

6.4.10 Glassware Cleaning Procedure

The glassware will be cleaned using the procedures outlined in Appendix B, section 4.3.

## 7. REAGENTS AND STANDARD SOLUTIONS

### 7.1 Column Chromatography Reagents

7.1.1 Alumina Woelm B, (Woelm Pharma) activated at 130°C for 48 h or longer.

7.1.2 Silica Gel

High purity grade, type 60, 70/230 mesh; extract the silica gel in a Soxhlet apparatus with methylene chloride for 10 h (minimum of two cycles per h). Air dry and activate by heating in a foil-covered glass container for at least 24 h at 130°C.

7.1.3 Silica gel impregnated with 40% (by weight) sulfuric acid. Add 2 parts (by weight) concentrated sulfuric acid to 3 parts (by weight) silica gel (extracted and activated) in a glass screw cap bottle. Tumble for 5 to 6 h, shaking occasionally until free of lumps.

7.1.4 Sulfuric Acid, Concentrated; ACS grade, specific gravity 1.84.

7.2 Sodium sulfate, granular, anhydrous. Extract with methylene chloride for 16 h (minimum of 2 cycles per h), air dry and then muffle for longer than 4 h; in a shallow tray at 400°C. Let cool in a desiccator and store in a 130°C oven.

### 7.3 Solvents

High purity, distilled in glass; methylene chloride, hexane, diethyl ether, acetone and isooctane. High purity solvents are dispensed from teflon squirt bottles.

7.4 Concentration Calibration Solutions

Three Chloroparaffin standard materials (Paroil 142, Paroil 152, and Paroil 1160) are required. Portions of the standards are accurately weighed and dissolved in isooctane to produce concentration calibration solutions at the concentrations shown in Table 7.1.

## 8. GC/MS PERFORMANCE CRITERIA

Single run limited mass range selected ion monitoring analyses of the chlorinated paraffins are carried out with the instrumental conditions and parameters outlined in Table 8.1. Eleven mass ranges, given in Table 8.2 are monitored during each run.

8.1 Tuning and Mass Calibration

The mass spectrometer is tuned on a daily basis prior to sample analysis using perfluorotributylamine (FC-43). For reproducibility of the relative abundance measurements, the abundance ratio of the m/z 414: m/z 633 ion will be adjusted to 1:3 (± 10%).

8.2 Initial Calibration for Clorinated Paraffin Analysis

Initial calibration is required before any samples are analyzed for chlorinated paraffins. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 8.3.

8.2.1 Tune and calibrate the instrument with FC-43 as outlined in Section 8.1.

8.2.2 The five concentration calibration solutions listed in Table 2 will be analyzed for the initial calibration phase.

8.2.3 Using the HRGC and MS conditions in Table 8.1 and the SIM monitoring parameters given in Table 8.2, analyze 1 µL of each of the five concentration calibration solutions.

8.2.4 Compute the response factors for each mass range using the computational method in Section 14.2.

8.2.4 Calculate the mean RF and the standard error.

8.3 Criteria for Acceptable Initial Calibration

8.3.1 The standard error of the mean RFs for the five calibration standards must be less than 30%.

Table 7.1. Concentration Calibration Solutions

| CP | Concentration in calibration solutions (μg/mL) | | | | |
|---|---|---|---|---|---|
| | CS1 | CS2 | CS3 | CS4 | CS5 |
| Paroil 142 | 100 | 50 | 20 | 10 | 1 |
| Paroil 152 | 100 | 50 | 20 | 10 | 1 |
| Paroil 1160 | 100 | 50 | 20 | 10 | 1 |

Table 8.1. HRGC/NCIMS Operating Conditions for CP Analysis

| | |
|---|---|
| **Mass spectrometer** | |
| Mode: | negative chemical ionization |
| Ionization gas: | methane |
| Ionizer pressure: | 0.7 torr |
| Electron energy: | 70 eV |
| Emission current: | 0.3 mA |
| Electron multiplier voltage: | -1700 V |
| SEV: | $10^{-7}$ |
| Source temperature: | 170°C |
| Overall SIM cycle time: | 3 s |
| **Gas chromatograph** | |
| Column coating: | DB-5 |
| Film thickness: | 0.25 μm |
| Column dimensions: | 30 m x 0.25 mm ID |
| Helium linear velocity: | ∿ 25 cm/s |
| Helium head pressure: | 8 psi |
| Injection type: | on-column |
| Injector temperature: | ambient |
| Interface temperature: | 300°C |
| Injection size: | 1 μL |
| Initial temperature: | 80°C |
| Initial time: | 2 min |
| Temperature program: | 80°C to 320°C at 10°C/min |

Table 8.2. SIM Mass Ranges for CP Analysis

| Mass range | Nominal scan time (s) | CP cell |
|---|---|---|
| 324-329 | 0.34 | C10-C12 |
| 359-364 | 0.34 | |
| 367-372 | 0.34 | |
| 393-401 | 0.34 | |
| 401-420 | 0.35 | C14-C17 |
| 441-454 | 0.34 | |
| 477-488 | 0.36 | |
| 498-503 | 0.36 | C20-C30 |
| 514-518 | 0.34 | |

8.3.2 The SIM traces for all ions used for quantitation must present a signal-to-noise (S/N) ratio of ≧ 3.

8.4 Routine Calibration

Routine calibration must be performed at the beginning of every day before actual sample analyses are performed and after all samples for the day are analyzed. Additional calibration during the day may be employed if instrument instability is suspected.

8.4.1 Inject 1 μL of concentration calibration solution CS2 as the initial calibration check on each analysis day.

8.4.2 Compute the RF for each ion range in the concentration calibration solution.

8.5 Criteria for Acceptable Routine Calibration

8.5.1 The measured RF for all cells must be within ± 30% of the average mean calculated in section 8.1.6.2.

8.5.2 If this criterion is not met, a second attempt will be made before repeating the entire initialization process.

9. QUALITY CONTROL PROCEDURES

9.1 Summary of QC Analyses

9.1.1 Initial and routine calibration and instrument performance checks.

9.1.2 Analysis of a batch of samples with accompanying QC analysies: up to 10 environmental samples of one matrix type plus QC analyses including one method blank, and one spiked blank. Additional QC samples, including field spikes, field blanks, trip spikes and trip blanks may be included in a batch of samples.

9.2 Performance Evaluation Solutions

Prior to sample analysis, a solution provided by the work assignment quality control cooridinator containing known amounts of chlorinated paraffins will be analyzed. The accuracy of measurement for performance evaluation samples should be in the range of 70-130% of true value.

9.3 Laboratory Method Blanks

A minimum of one laboratory method blank is generated with each batch of samples. A method blank is generated by performing

all steps detailed in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. For sediment, suspended solids, and biota samples, the matrix is omitted. Deionized water is substituted for environmental water.

9.3.1 An acceptable method blank exhibits no positive response in the characteristic ion ranges monitored.

9.3.1.1 If the above criterion is not met, solvents, reagents, apparatus, and glassware are checked to locate and eliminate the source of the contamination before any further samples are extracted and analyzed.

9.3.1.2 If new batches of reagents or solvents contain interfering contaminants, they will be purified or discarded.

9.4 Spiked Samples

9.4.1 Method Spikes

A minimum of one method spike is generated with each batch of samples. A method spike is generated by performing all steps detailed in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. For sediment, suspended solids, and biota samples, the matrix is omitted. Deionized water is substituted for environmental water. These samples are spiked with known amounts of chlorinated paraffins prior to extraction.

9.4.2 Field Spikes

Field spikes will be analyzed using the method at the frequency specified in the experimental design contained in the main body of the QAPP.

9.4.3 Trip Spikes

Trip spikes will be analyzed using this method at the frequency specified in the experimental design contained in the main body of the QAPP.

## 10. SAMPLE PRESERVATION AND HANDLING

Water and sediment samples will be maintained at 8°C or lower until extraction. Mussel samples will be maintained at -20°C until extraction. Sample extracts will be stored at 8°C or less until analysis.

## 11. SAMPLE PREPARTION AND EXTRACTION

### 11.1 Extraction of Water Samples

11.1.1 Filter water through a 0.45 μ filter (Type HA, Millipore, 47 mm) in a millipore filtration apparatus. Use a 2 L suction flask to receive the filtrate. Use suction by aspiration to facilitate the process.

11.1.2 Rinse the sample jar with a 250-mL portion of the filtrate and pass through the filter again. Note: For samples with a large amount of particulate, more than one filter may be needed if filtration becomes slow.

11.1.3 Measure the volume of the filtrate in a 500-mL graduated cylinder and pour back into the sample jar.

11.1.4 Transfer the filter to a clean 4 oz jar using forceps.

11.1.5 Transfer 1000 mL of the filtrate into a 2-L separatory funnel.

11.1.6 Add 60 mL of hexane, stopper, invert and vent the funnel. Shake the funnel for 2 min vigorously enough to form an emulsion.

11.1.7 Allow the phases to separate, drain the aqueous phase into a 1000-mL Erlenmeyer flask and the hexane phase into a 250-mL Erlenmeyer flask.

11.1.8 Transfer the aqueous phase back into the 2-L separatory funnel and add another 60 mL of hexane to the 1000 mL Erlenmeyer to rinse the flask. Add the rinse to the separatory funnel and shake again for 2 min.

11.1.9 Repeat step 11.1.7.

11.1.10 Discard the aqueous phase.

11.1.11 Add enough anhydrous sodium sulfate to the hexane extract to remove the water (10-20 g).

11.1.12 Transfer the hexane extract to a 250-mL Kuderna Danish (KD) flask equipped with either a 5- or 10-mL receiver. Complete the transfer with three rinses of hexane, 10-20 mL each.

11.1.13 Add several carborundum chips and place a 3-ball Snyder column into position.

11.1.14 Concentrate the hexane to about 5 mL on a steam bath.

11.1.15 Transfer the concentrated hexane extract to a 4-dram vial using a pasteur pipette. Complete the transfer with three rinses of hexane (about a0.5 mL each).

11.1.16 Proceed to the sulfuric acid/silica cleanup (Section 12.1).

11.2 Extraction of Sediment Samples

11.2.1 Transfer the sediment sample (~ 1 kg) to a clear pyrex baking dish (12 in x 12 in x 2 in) with a stainless steel spatula.

11.2.2 Drain and discard the excess water.

11.2.3 Dry the sediment by placing in an oven (65-70°C) for 48-60 h. Stir the sediment occasionally to facilitate drying and to break up large clumps.

11.2.4 Break the sediment into a fine powder using a mortar and pestle if necessary. Remove large rocks with a pair of forceps.

11.2.5 If necessary, sift the sediment through a screen to remove particles greater than 1 mm.

11.2.6 Weigh 100 g (+/- 0.1 g) of the sediment into a clean 8 oz jar.

11.2.7 Add 100 g (+/- 0.1 g) of anhydrous sodium sulfate to the sediment sample and mix with a spatula.

11.2.8 Load the sediment/sodium sulfate mixture into a Soxhlet flask containing a pad of glass wool.

11.2.9 Add 200 mL of hexane to a 200-mL round bottom flask, add several carborundum chips and extract the sample for 16 h.

11.2.10 Allow the apparatus to cool and manually cycle any remaining hexane in the sediment. Remove the 250-mL flask from the apparatus. Discard the sediment.

11.2.11 Transfer the hexane to a 250-mL KD flask. Complete the transfer with three 10-mL rinses of hexane. Concentrate to about 5 mL and transfer to a 4-dram vial using a Pasteur pipette. Complete the transfer with three 0.5-mL rinses of hexane. Cap with a teflon®-lined lid.

11.2.12 Proceed to the sulfuric acid/silica cleanup (Section 12.1).

## 11.3 Preparation and Extraction of Mussel Samples

11.3.1 Open the mussel with a sharp knife by cutting the muscles attached to the shell next to the hinge.

11.3.2 Scrape and transfer the tissue to a tared 500-mL beaker.

11.3.3 Drain off any residual water and remove any plant tissue.

11.3.4 Open and add enough mussels to obtain at least 100 g of tissue.

11.3.5 Homogenize the tissue in a Waring blender. A homogeneous viscous liquid should be obtained.

11.3.6 Transfer the tissue homogenate to a clear pyrex dish (12 in x 12 in x 2 in) using a stainless steel spatula.

11.3.7 Slowly add 3 times the sample weight of anhydrous sodium sulfate to the homogenate, stirring frequently with a spatula.

11.3.8 Allow the mixture to dry until it is free flowing. This step may take several days.

11.3.9 Load the tissue/sodium sulfate mixture into a Soxhlet flask to an equivalent weight of 100 g of mussel tissue. Extract for 16 h with 450 mL of hexane.

11.3.10 Cool and remove the round bottom flask. Discard the tissue/sodium sulfate mixture.

11.3.11 Add 10-20 g of anhydrous sodium sulfate to dry the extract.

11.3.12 Add 20 g of 40% (w/w) sulfuric acid on silica gel, and let stand for 1 h with occasional swirling.

11.3.13 Transfer the extract to a 250-mL KD flask. Complete the transfer with three 20-mL rinses of hexane. Concentrate to about 5 mL.

11.3.14 Transfer the concentrated extract to 4-dram vial. Complete the transfer with three 0.5-mL rinses of hexane.

11.3.15 Concentrate the extract to about 0.5 mL with a gentle stream of nitrogen. Cap with a teflon-lined lid.

11.3.16 Proceed to the alumina cleanup step. (Section 12.2.)

## 12. CLEANUP PROCEDURES

### 12.1 Sulfuric Acid/Silica Cleanup

12.1.1 Prepare the columns (champagne minicolumns with 30-mL reservoir, Supelco Inc.) by inserting a small pad of pesticide-grade glass wool (DCMS treated, Alltech Associates).

12.1.2 Rinse the columns and glass wool with three aliquots each of acetone and hexane in that order.

12.1.3 Add 1.0 g of 40% (w/w) sulfuric acid/silica to the column. Layer about 1 cm of anhydrous sodium sulfate on top of the bed.

12.1.4 Wet the column with enough hexane to saturate the bed. DO NOT ALLOW THE COLUMN TO DRAIN FAR ENOUGH TO EXPOSE THE BED OF SILICA.

12.1.5 Transfer the sample to the column using a pasteur pipette. Complete the transfer with three 0.5-mL rinses of hexane. Collect the eluent in a 6-dram vial.

12.1.6 Allow the sample extract to flow through the column and add 5 mL of hexane to the column.

12.1.7 Allow the column to run dry and rinse the tip with about 1 mL of hexane into the vial.

12.1.8 Concentrate the eluate to about 0.5 mL with a gentle stream of nitrogen. Cap with a teflon®-lined lid.

### 12.2 Alumina Cleanup

12.2.1 Prepare the columns as described for the sulfuric acid/silica columns (Section 12.1.1). Use 1.0 g of basic alumina prepared as described in Section 7.1.1.

12.2.2 Wet the column with enough hexane to saturate the bed. DO NOT ALLOW THE SOLVENT LEVEL TO FALL BELOW THE TOP OF THE ALUMINA BED.

12.2.3 When the solvent level has reached the bed, add the sample extract with a pasteur pipette.

12.2.4 Measure 10 mL of 1% (v/v) diethyl ether in hexane into a graduated cylinder. Complete the transfer of the sample extract to the column with three rinses of the 1% ether in hexane mixture when the sample extract has

completely drained into the alumina bed. Add the remaining 1% ether in hexane. Collect the eluate in a 4-dram vial.

12.2.5 When the 1% ether in hexane has reached the top of the bed, add 10 mL of 50% diethylether in hexane to the column. Collect the eluate in a fresh 4-dram vial. Discard the 1% ether eluate.

12.2.6 After the 50% ether in hexane fraction has completely eluted and the column drained dry, rinse the tip of the column with about 1 mL of hexane and concentrate the sample to about 0.5 mL with a gentle stream of nitrogen.

12.2.7 Transfer the sample with a pasteur pipette to a 2-mL conical reaction vessel (Supelco). Complete the transfer with one rinse of hexane and two rinses of acetone (about 0.5 mL each). Reduce the sample to dryness with a gentle stream of nitrogen.

12.2.8 Cap with a teflon®-lined lid and store for analysis by mass spectrometry.

12.2.9 Prior to analysis, the analyst will add a 50 µL (or other volume) aliquot of isoctane to the sample and sonicate for 30 sec.

## 13. INSTRUMENTAL PROCEDURES

13.1 Once routine calibration criteria are met, the instrument is ready for sample analysis. Prior to the first sample, a blank injection of isooctane will be analyzed to document system cleanliness. If any evidence of system contamination is found, corrective action must be taken and another isooctane blank analyzed.

13.2 The typical daily sequence of injections is shown in Table 13.1.

## 14. DATA REDUCTION

In this section, the procedures for data reduction are outlined for the analysis of chlorinated paraffins in environmental samples.

### 14.1 Quantitative Calculations

#### 14.1.1 Calculation of Response Factors

Response factors for each mass range are calculated from the data obtained during the analysis of concentration calibration solutions using Equation 14.1.

Table 13.1. Typical Daily Sequence for CP Analysis

| | |
|---|---|
| 1. | Tune and calibrate mass spectrometer with FC-43. |
| 2. | Inject concentration calibration solution. |
| 3. | Inject isooctane blank. |
| 4. | Inject samples. |
| 5. | Inject concentration calibration solution. |

$$RF = \frac{Astd}{Cstd \times Vstd} \qquad \text{EQ. 14.1}$$

Where:
Astd is computer generated area for a mass range
Cstd is the concentration of the standard (ng/μL)
Vstd is the volume of sample injected in (μL)

14.1.2 Calculation of Chlorinated Paraffin Concentrations

Chlorinated paraffin concentrations will be calculated for each mass range using Equation 14.2.

$$\text{Concentration (ppb)} = \frac{Aex \times Vex}{RF \times Vinj \times M} \qquad \text{EQ. 14.2}$$

Where:
Aex is the computer generated area of the mass range in the extract
RF is the response factor calculated in Equation 14.1
Vinj is the volume of extracted injected (μL)
Vex is the final volume of the extract (μL)
M is the mass of sample taken for analysis (g)

14.2 Estimated Method Detection Limit

Estimated method detection limits must be calculated in situations where (1) no response is noted for a specific mass range and (2) where a response is quantitated as a trace value, that is, where the response is between 3 and 10 times the signal to noise ratio. These two cases are discussed below.

14.2.1 For samples in which no signal is detected above the baseline, calculate the estimated minimum detectable concentration. The background $\sigma$ is determined by integration the ion abundances for the mass ranges in the appropriate regions and relating the area to an estimated concentration that would produce that area. The formula is given in Equation 14.3.

$$EDL = \frac{3 \times Aex \times Vex}{RF \times Vinj \times M} \qquad \text{EQ. 14.3}$$

Where:
EDL is the estimated detection limit (ppb)
Aex is the computer generated area of the mass range in the extract
RF is the response factor calculated in Equation 14.1
Vinj is the volume of exract injected (μL)
Vex is the final volume of extract (μL)
M is the mass of sample taken for analysis (g)

14.2.2 If a response for a specific mass range is quantated as a trace value [signal to noise is greater than or equal to 3 ($\sigma$) but less than 10 ($\sigma$)], the analyst must also provide an estimated method detection limit. This is accomplished by using the average observed signal to noise on either side of the response and calculating as given in Equation 14.3.

## 15. REPORTING AND DOCUMENTATION

Data will be reported for each individual sample. Concentration values or estimated detection limits will be reported for each mass range monitored. Raw data, calculations, etc, will be maintained in a format as to allow a complete external data reviewed.

# APPENDIX D

## VALIDATION PROCEDURES FOR THE ANALYTICAL METHOD

# APPENDIX D -- TABLE OF CONTENTS


| SECTION | HEADING | REVISION | DATE |
|---|---|---|---|
| 1.0 | Summary | | 11/18/86 |
| 2.0 | Experimental Design | | 11/18/86 |
| 3.0 | Analytical Procedures | | 11/18/86 |
| 4.0 | Data Reduction | | 11/18/86 |
| 5.0 | Data Quality Assessment | | 11/18/86 |

## 1.0 Summary

The method validation phase of this work was designed to assess the precision, accuracy, and recovery of the method. Matrix samples, (except mussel tissue, which was obtained commercially) for the validation were obtained from Sugar Creek (Dover, Ohio) sampling stations A and B during a reconnaissance trip conducted on August 12, 1986. Station A is located downstream from the Dover Chemical Plant and station B is located upstream. Station B samples provided the basis for method assessment, while station A samples were run to obtain a preliminary indication of downstream CP levels.

## 2.0 Experimental Design

The experimental design for the method validation phase of this study is outlined in Table 2.1. The design is broken down into two phases. The first phase was designed to measure background (L0) levels of CPs in the matrices, and to provide a basis for setting spiking levels (L1 - L3) for phase II. The phase II analyses were used to assess method accuracy, precision, and recovery. A batch of samples consists of four validation samples and associated quality control samples. A laboratory method blank and a spiked control sample for water and a laboratory method blank for sediment have been incorporated. Since a control sediment was not available, spiked control sediments were not included in the design.

## 3.0 Analytical Procedures

The validation samples were analyzed according to the procedures detailed in Appendix C.

## 4.0 Data Reduction

Data will be reduced according to the procedures outlined in Appendix C.

## 5.0 Data Quality Assessment

Precision, accuracy and recovery will be determined for three spiking levels for each of the three cells.

### 5.1 Precision

Precision will be assessed as relative standard deviation within each cell. Precision will be expressed as relative standard deviation as defined in Section 9.1 of the QAPP.

TABLE 2.1

22-Aug-86 MRI PROJECT No. 8853-A(01)--CHLOROPARAFFINS

METHOD VALIDATION

A : WATER

| PHASE | Batch No. | (upstream) "B" Pool L0 | (downstream) "A" Pool L0 | L1 | L2 | L3 | Method Blank (distilled water) S0 | Spike Control (distilled water) S1 |
|---|---|---|---|---|---|---|---|---|
| I | 1 | 2X | 2X | - | - | - | 1X | 1X |
| II | 2 | - | 1X | 1X | 1X | 1X | 1X | 1X |
| II | 3 | - | 1X | 1X | 1X | 1X | 1X | 1X |
| II | 4 | - | - | 1X | 1X | 1X | 1X | 1X |
| Total # of analyses: | | 2 | 4 | 3 | 3 | 3 | 4 | 4 |

B : SEDIMENT

| PHASE | Batch No. | (upstream) "B" Pool L0 | (downstream) "A" Pool L0 | L1 | L2 | L3 | Method Blank (no sediment) S0 |
|---|---|---|---|---|---|---|---|
| I | 5 | 2X | 2X | - | - | - | 1X |
| II | 6 | - | 1X | 1X | 1X | 1X | 1X |
| II | 7 | - | 1X | 1X | 1X | 1X | 1X |
| II | 8 | - | - | 1X | 1X | 1X | 1X |
| | Total | 2 | 4 | 3 | 3 | 3 | 4 |

Note 1 : 1X = single analysis ; 2X = replicate analyses.

Note 2 : Each sample in the above table , whether in the matrix (e.g., riverwater or sediment) or not, will go through the extraction process.

Note 3 : One solvent blank and one calibration check at the the L2 spiking level will be run per day for instrument check.

Note 4 : Spiking level S1 for the distilled water spike check will be 10 times the estimated LOQ (i.e., 5 ppb for water).

## 5.2 Accuracy

The accuracy of the method will be assessed within each cell. Accuracy will be expressed as A% as defined in Section 9.2 of the QAPP.

## 5.3 Recovery

Recovery will be assessed within each cell. The measure of recovery will be percent recovery as defined in Section 9.3 of the QAPP.

# APPENDIX E

# PEI QUALIFICATIONS

PEI Associates, Inc.

LESLIE J. UNGERS, C.I.H.
Senior Staff Expert

EDUCATION:

B.A., Zoology, Miami University, 1973
M.S., Industrial Hygiene, College of Medicine, University of Cincinnati, 1984

PROGRAM QUALIFICATIONS:

- Certified Industrial Hygienist
- Senior Industrial Hygienist for PEI specializing in protection, surveillance and monitoring of workers handling hazardous wastes and toxic substances
- Experienced in the collection of water sediment, biota and other limnological samples.
- Experienced in the management of field studies involving chain of custody and sample QA
- Working knowledge of EPA and OSHA regulations and NIOSH recommendations as they apply to the ambient and work environment

RELEVANT EXPERIENCE:

Mr. Ungers is a Board-Certified Industrial Hygienist (No. 2302) with more than 12 years of experience in the identification, evaluation, and control of workplace and environmental hazards. As Group Leader of PEI Associates' Risk Assessment Group, he is responsible for managing and conducting industrial risk assessment projects and audits for both the government and the private sector. He is an adjunct professor at the University of Cincinnati, College of Mathematics and Applied Sciences. He is a full-member of the American Industrial Hygiene Association and a member of the American Academy of Industrial Hygiene.

Field Investigations

Mr. Ungers has directed a number of investigations and chemical reviews for the U.S. Environmental Protection Agency's Office of Toxic Substances. He has been instrumental in promoting the success of the EPA's interagency efforts with NIOSH. His past experience in conducting field investigations of water and sediment quality at inland lakes and streams, conducting NIOSH surveys and control technology efforts has been helpful to EPA in its formulation of cost-effective industry-specific investigations. Several years ago, Mr. Ungers was instrumental in assisting OTS with the development of a methodology assessing the relative importance of toxic chemicals.

Leslie J. Ungers (continued)

Industrial Site Surveys

Mr. Ungers has conducted over 200 site surveys. These efforts have allowed him to gain an understanding of a wide range of chemical and manufacturing operations, including inorganic minerals processing, paint and surface coating formulation, organic chemical manufacturing, food processing, microelectronics, and semiconductor fabrication. His experience in these industries has focused on the identification of potentially hazardous unit operations that may contribute to the release of toxic substances into the workplace or surrounding environment and result in real or potential violations of OSHA Health and Safety Standards.

Industrial Hygiene

Mr. Ungers has conducted industrial hygiene monitoring at a variety of industrial processes. This experience includes monitoring workers for exposures to organic solvents (e.g., methyl ethyl ketone, butyl acetate, benzene, xylene) at paint manufacturing operations. He has also assessed worker exposure to a number of toxic substances, including organic solvents, toxic gases, and flammable and pyrophoric gases. This work has required him to determine the sources of occupational exposure and to define worker activities prior to establishing a monitoring scenario. During these investigations Mr. Ungers has been responsible for ensuring the quality of sampling data collected in the field. Mr. Ungers' OTS-related experience in this area includes using his industrial field experience in estimating potential routes of exposure to workers involved in processes for which little or no monitoring data are available.

# THOMAS J. WAGNER

EDUCATION:

Five years graduate work toward Ph.D. in Analytical Chemistry, University of Minnesota, 1971
B.A., Chemistry, Thomas More College, 1966

QUALIFICATIONS:

Mr. Wagner has over 20 years' experience in analytical chemistry and 8 years in technical project management. He has been with PEI for 8 years. For the past 7 years he has served as the Quality Assurance Coordinator for the Environmental Measurement Division. Previously he was Project Manager and Senior Group Chemist. In the past, he has taught analytical chemistry and instrumental analysis at the University of Cincinnati. Mr. Wagner has an extensive background in both wet chemical methods and instrumental techniques such as atomic absorption, gas chromatography, ion chromatography, infrared spectroscopy, nuclear magnetic resonance, and mass spectroscopy. He is a member of the American Chemical Society, including both the Analytical and Environmental Divisions.

RELEVANT EXPERIENCE:

Quality Assurance

As Quality Assurance Coordinator, Mr. Wagner has served as Quality Assurance Officer for two previous SSCD (DSSE) contracts. When required for these previous contracts, he has developed and monitored the QAPP's under the "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS 005/80," which included plans for the testing of a Solid Waste Reduction Plant for Washington, D.C., and VE observations during Stationary Source Inspections and Test Observations. Mr. Wagner has revised the quality assurance plan for PEI's laboratory, written quality assurance plans for the Emission Measurement Group and Ambient Monitoring Group, written chain-of-custody procedures for sampling and analysis, and administered performance audit programs. He has also written sections in Volumes 2 and 3 of the U.S. EPA "Quality Assurance Handbook for Air Pollution Measurement Systems," and conducted quality assurance and VOC sampling and analysis workshops for government personnel and private contractors.

Mr. Wagner is Program Manager for PEI's contract for Quality Assurance Technical Support to the Water Engineering Research Laboratory (WERL). Under this contract he has conducted numerous Technical System Audits and Data Quality Audits nationwide and directed the development of a "Quality Assurance Procedures Manual for WERL Project Officers."

Source Testing

Mr. Wagner has participated in the project design and developed and monitored QAPP's for the Collaborative Test of EPA Method 6B, the Air Curtain Hood Test

Thomas J. Wagner (continued)

Program at the Asarco Copper Smelter in Tacoma, a full-scale scrubber characterization study of large utility boilers, the Comparison Study of EPA Methods 16 and 16A, the Comparison Study of EPA Methods 15 and 15A, Development of a Source Test Method for Chromium Speciation, and the Comparison study of EPA Method 5, 5B, and 5F for fluidized catalytic Cracking units and oil burning utilities boilers. Mr. Wagner assisted in the design and was the QA Officer for the laboratory and field validation studies of the Volatile Organic Sampling Train (VOST).

Field Monitoring and Analytical Support

Mr. Wagner has participated in the project design and developed and monitored QAPP's for the Philadelphia Aerosol Field Study, the Toxicity Treatability Assessment of Iron and Steel Industry Wastewaters, Assessing Hazarous Waste Contamination of Locally Grown Agricultural Products, and the ambient air monitoring during the hazardous waste cleanup at the Chem-Dyne site. He has managed projects involving the evaluation of new analytical techniques for screening ambient particulate samples for polynuclear aromatic hydrocarbons and the development of an alternate analytical procedure for EPA Method 5F. Mr. Wagner is the Quality Assurance Officer for a toxic monitoring project for an industrial client. This project involves the monitoring of two inorganic and five organic compounds in the ambient air at five sites. As a senior staff chemist, he improved the technique for trace metal analyses by atomic absorption in solid waste leachate samples and developed a method for measuring hydrocarbon emissions from a stationary source. He also supervised the laboratory effort for a full-scale scrubber characterization study involving both trace organic and trace metal analyses in gaseous, liquid, and solid effluents.

Technical Support

Mr. Wagner has developed lectures for workshops on quality assurance for emission testing based on Volume III of the Quality Assurance Handbook for Air Pollution Measurement Systems: Stationary Source Specific Methods and for VOC Sampling and Analysis Workshop, EPA-340/1-84-001b. He has also prepared lectures for advanced training and special topics in emission testing workshops. Mr. Wagner has participated in the presentation of 18 workshops nationwide and has presented papers at national symposia, including the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants.

PEI Associates, Inc.

# Thomas A. Janszen

EDUCATION: B.S., Biology, Rockhurst College, 1972
M.S., Biology, Old Dominion University, 1974

RELEVANT EXPERIENCE:

Mr. Janszen is a Group Leader and a Project Director/Manager in PEI's Waste Management Division with more than 11 years of experience. Mr. Janszen was the project manager for collecting mollusk samples over a three-mile section of the Ohio River near Cairo Illinois. Mr. Janszen was the project manager and lead field sampler for collecting monthly water and sediment samples over a period of two years from a lake in Virginia Beach, Virginia. Mr. Janszen also collected extensive numbers of sediment samples from the Great Dismal Swamp over a one year period.

During the past eight years, he has managed or played a key technical role in over 40 solid and hazardous waste projects totaling over $3,000,000. Mr. Janszen is the project manager for preparing three chemical agent treatment and storage RCRA Part B's for the Department of Defense. He is also the project manager for preparing a RCRA Part B for one of the nation's largest offsite industrial hazardous waste storage and treatment facilities. Mr. Janszen was directly responsible for the design of the container storage area at this facility, which will store as many as 13 different types of incompatible waste at one time. Mr. Janszen was also responsible for the complete design of an indoor hazardous waste pile to be operated at this facility. This particular facility will also be permitted to store and treat almost all hazardous wastes listed in 40 CFR 261.

Mr. Janszen is currently directing the performance of 150 liability audits of hazardous waste TSD facilities around the United States for DOE. Mr. Janszen is also PEI's key senior advisor on a RCRA Subtitle D implementation project being performed for OSW. Mr. Janszen was the Quality Assurance Officer for a RCRA Part B developed for a high-technology computer firm. He performed over 50 technical reviews of Part B applications (including 15 land disposal facilities). Mr. Janszen has also managed the development and presentation of land disposal RCRA Part B workshops across the country. These workshops were presented to Federal and state agency personnel and industrial personnel. Additionally Mr. Janszen has developed hazardous waste training programs for several industrial clients who manage hazardous wastes. He also assisted in the development of a model Part B application to be used in workshops and seminars for industry and EPA.

Mr. Janszen's more than 100 site inspections at a wide variety of industrial facilities have involved evaluations of facility compliance and assessments of technology related to hazardous waste handling, treatment, storage, and disposal procedures; fugitive dust control; air pollution control; and volatile organic compounds. He has also conducted interim status inspections at land disposal facilities.

Thomas A. Janszen (continued)

Mr. Janszen played a key technical role in PEI's development of the most extensive and detailed Part B checklist used for reviewing Part B's for completeness and technical adequacy. This checklist is now widely used by many U.S. EPA Regions and many state agencies.

PEI Associates, Inc.

# ROBERT L. HOYE

EDUCATION:

B.S., Zoology, Ohio University, 1974
M.S., Environmental Science, University of Cincinnati, 1979

RELEVANT EXPERIENCE:

Mr. Hoye is a Group Leader in PEI's Waste Management Division. He has 9 years of experience in conducting RCRA related solid and hazardous waste management studies and assessments. Mr. Hoye has acted as Project Manager, Task Manager, and/or principal researcher on projects dealing with data base development, industry wide solid waste assessments, waste characterization studies, environmental monitoring of groundwater and surface waters, evaluation of solid and hazardous waste management practices, development of multimedia sampling and analysis protocols and manuals, and the impact and costs of existing and alternative waste control technologies. Mr. Hoye has managed or conducted over 100 site inspections and sample acquisition visits throughout the country and managed ground water and surface water monitoring at eight waste disposal facilities.

Mr. Hoye recently managed a study for EPA's Office of Radiation Programs to estimate radon-222 emissions and associated health risks from uranium mills and associated tailings piles. As part of this effort he is preparing a Background Information Document (BID) in support of EPA regulations that will be promulgated. He also completed a study of heap leaching of gold ores with cyanide which focused on conceptual control practices.

During past projects Mr. Hoye developed and implemented sampling plans, data management systems, QA/QC plans including field sampling protocols, following EPA guidelines (SW-846). He managed the installation of groundwater and surface water monitoring stations and collection of periodic samples at several sites. He is familiar with DOT regulations and EPA guidelines pertaining to shipping of environmental and hazardous waste samples.

Mr. Hoye was Project Manager of a waste characterization and industry overview study of the nonferrous smelting and refining industry. This large volume waste related study, conducted for EPA-OSW in response to RCRA, involved site investigations, sample collection, and waste characterization at 24 facilities. Mr. Hoye was Assistant Project Manager of a RCRA-mandated multi-million-dollar multi-year study of solid waste and disposal technology in the mining industry. During this project, Mr. Hoye conducted surveys of waste disposal technologies, managed waste characterization sampling studies at over 65 sites and assessed environment impacts by conducting eight case studies that involved groundwater and surface water monitoring. This study also included evaluation of control technologies and the cost associated with these ancillary/mitigative practices.

Mr. Hoye managed hydrological assessment of two waste disposal impoundments for the Bureau of Mines. In addition, he has conducted assessments of municipal waste collection and disposal systems in several midwestern cities. Mr. Hoye has experience in conducting limnological field studies including collection of fish by electroshocking, nets, rotenone, and collection of benthos and sediment samples.

# BARBARA B. LOCKE

EDUCATION:

M.S., Environmental Science, Indiana University, 1983
B.A., Biology, Stephens College, 1980

RELEVANT EXPERIENCE:

Ms. Locked has over 4 years experience in sampling hazardous wastes and other environmental media. She sampled lake sediments on the Great Lakes to determine outfall compliance while employed with the EPA-Great Lakes National Program Office. As part of this effort she utilized an Ekman Dredge, Ponar Dredge, and Core Sediment sampling equipment in industrial harbor areas of the Great Lakes. She collected the samples, packaged them for shipment, utilized EPA chain-of-custody procedures and wrote up trip reports containing exact sample locations to be used in enforcement proceedings. Furthermore, Ms. Locke sampled stream sediments for possible radiation contamination around a DOE facility in Wedon Springs, Missouri. She selected the sample locations, collected the samples, and wrote the subsequent report of results. Ms. Locke also conducted a pre-strip mining environmental assessment in which she collected water, soil, sediment, flora and fauna samples. Additionally, she performed stream transects, volumetric flow measurements, and collected groundwater samples. She has collected soil samples suspect of TCDD and PCB contamination and she conducted several field investigations to check for leaking underground petroleum storage tanks. She is thoroughly familiar with the use of personal protective equipment levels B, C, and D.

As a member of the cleanup crew on a $1.2 million emergency Superfund site in Gary, Indiana, Ms. Locke developed and implemented a sampling and analysis plan involving the cleanup of over 65,000 drums. In this capacity, she was responsible for the sampling (including compositing operations), record-keeping, chain-of-custody, manifesting, transportation, and disposal of all waste and waste samples. Under the same EPA contract, Ms. Locke has served as Response Manager and Site Engineer for several emergency cleanup operations.

As part of a State-initiated study, Ms. Locke recently completed an in-depth analysis of delisting hazardous wastes under the RCRA regulations. She evaluated the history of delistings granted and the future potential (under the 1984 Solid Waste Amendments) for delisting specific wastes. Also under this study, she evaluated proposed alternative treatment technologies for the metal plating industry. The evaluation included cost considerations, technical feasibility, and market research.

Ms. Locke was been extensively involved with hazardous waste management under RCRA and CERCLA for the last 3 years. She was responsible for coordinating and writing major portions of Part B applications for 6 multi-operating TSD facilities,including incinerators, landfills, waste piles, surface impoundments, and container and tank storage. Furthermore, she recently completed an independent audit for one of the largest hazardous waste landfills in the

Barbara B. Locke (continued)

county. As part of this effort, she completed on-site inspections and record reviews of the operating procedures. The result of this effort was a state ordered regulatory compliance report (including compliance with the 1984 Solid Waste Amendments). As a result of the 1984 Solid Waste Amendments, Ms. Locke recently revised and updated closure plans for partial closure (scheduled to begin immediately) of a commercial incineration facility. The plans included closure of 7 surface impoundments on outdoor container storage and waste pile area, and above- and below-ground storage tanks. She will continue to meet with State and Federal EPA personnel throughout the planned closure operations.

# JUDY L. MCARDLE

EDUCATION:

B.S.E., Environmental Engineering, Purdue University, 1983
B.S., Natural Resources and Environmental Science, Purdue University, 1983

RELEVANT EXPERIENCE:

Ms. McArdle is an environmental engineer in PEI's Waste Management Division with 3 years of experience in RCRA- and TSCA-related studies. As part of the EPA/OSW large-volume waste studies under Section 8002 of RCRA, Ms. McArdle helped prepare an industry profile of the copper smelting/refining industry. The profile provides data on the number, size, location, and operating status of smelters/refineries across the country as well as information on the volume, characteristics, and management of wastes generated by the industry. Data gathering efforts involved site visits, sample collection, and contact with trade associations and regulatory personnel. The information is being used by the EPA to develop regulatory strategies for wastes that are currently excluded from regulation under Subtitle C of RCRA.

Ms. McArdle is familiar with the use of the Kemmerer water sampler and the Ekman dredge through her involvement in water quality studies of the Wabash River and numerous lakes and streams in the West Lafayette, Indiana, area.

In support of contemplated regulatory action under TSCA, Ms. McArdle investigated occupational exposure to methyl chloride and chlorinated paraffins for EPA/OTS. These investigations involved preparation of industrial process descriptions, estimation of release rates and exposure levels, and evaluation of engineering controls. She has also worked with EPA/ORD's Exposure Assessment Group to gather information needed to assess occupational and public exposures to dioxin-related compounds. This effort entailed summarizing data on the physical, chemical, and biological properties of 15 of the most toxic congeners; identifying sources of these compounds in the environment; determining release rates; and enumerating exposed populations.

# MICHAEL M. AROZARENA

EDUCATION:

M.S. Environmental Sciences, University of Cincinnati, 1979
B.S., Natural Sciences, Xavier University, 1977

RELEVANT EXPERIENCE:

As an environmental scientist with PEI Associates, Mr. Arozarena has more than 7 years of managerial and technical experience in water/wastewater monitoring, groundwater monitoring, ambient air monitoring and hazardous waste management. Currently, Mr. Arozarena is managing a field monitoring project in Falls City, Texas, for EPA's Office of Radiation Programs (ORP) involving a comparison of several existing measurement methods for radon in soil gas. Sampling methods, including Lucas cell alpha scintillation counting, charcoal adsorption, and alpha track techniques, were compared in order to determine their ability to characterize the potential of any site to cause elevated indoor radon concentrations. In addition to the collection of soil gas samples, Mr. Arozarena collected soil samples to a depth of 10 feet for radium-226 analysis, soil moisture content, determination of radon emanating power, and diffusion coefficients.

Mr. Arozarena has also participated in numerous groundwater and surface water monitoring studies for EPA and industrial clients. He managed a groundwater monitoring study for a chemical manufacturing plant investigating the impact of a superfund landfill, and he has participated in several wastewater monitoring projects in fulfillment of NPDES permit application requirements. He monitored wastewater discharges from two steel facilities in central Ohio and prepared their applications. The most recent wastewater sampling project involved the monitoring of numerous electroplating/metal finishing operations for a major jet engine manufacturer in Cincinnati. Sampling and analysis supported a baseline monitoring report submitted in response to recently developed pretreatment regulations.

Mr. Arozarena has also collected hundreds of soil samples for EPA and industrial clients. An intensive soil sampling study was conducted in Texas to investigate lead and cadmium contamination of soil in the vicinity of secondary lead smelters. A large portion of the soil sampling studies for industrial clients were concerned with the proper closure or decontamination of surface impoundments under RCRA.

Recently, Mr. Arozarena completed an air radiation monitoring study for ORP in central Florida. Alpha track detectors, charcoal canisters, high-volume samplers, and particle sizing samplers were installed at five wet-process phosphoric acid plants operating phosphogypsum piles. Data was collected over a period of one year and will be used to evaluate the need for radionuclide emission standards for phosphogypsum piles. Mr. Arozarena has worked with ORP on several other projects. One study involved the completion of site-specific information on all active and inactive phosphogypsum piles in the United States. ORP used this information to determine exposure to

MICHAEL M. AROZARENA (continued)

radionuclides of residents in the vicinity of these piles. He assisted in the collection of groundwater, surface water and sediment samples at two chemical manufacturing facilities in Missouri that managed phosphogypsum piles. Finally, he provided assistance on an ORP study of radon emissions and control practices at active uranium mills and associated tailings piles.

He also served as field manager on several ambient air monitoring projects involving the collection of monitoring data to satisfy prevention of significant deterioration (PSD) permit requirements. These projects included the monitoring of total suspended particulates, carbon monoxide, sulfur dioxide, ozone, nitrogen dioxide, and meteorological parameters. He was involved in organizing an ozone monitoring study in the vicinity of Indianapolis, Indiana, and monitoring oxides of nitrogen, reactive hydrocarbons, and meteorological parameters in Jeffersonville, Indiana. Other past ambient air monitoring projects included field sampling of fugitive dust emissions from various coal mining operations as part of the development of emission factors, and field sampling of fugitive chrysotile asbestos emissions at a recreational area in California.

Prior to coming to PEI in 1979, he worked for over a year in drinking water research at U.S. EPA MERL in Cincinnati, Ohio. He conducted bench- and pilot-scale studies for the removal of parasites from drinking water using various water treatment processes including coagulation/flocculation/sedimentation, granular media filtration, and diatomaceous earth filtration.

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**7. Author(s)** Murray, Tom and Mary Frankenberry[a]; Steele, David H.[b]; Heath, Robert G[c]


**8. Performing Organization Rept. No.**


**9. Performing Organization Name and Address**

a) Exposure Evaluation Division. OTS
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c) Battelle Columbus Division, 2030 M St. N.W. Washington, D.C. 20036


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**15. Supplementary Notes**
Joseph J. Breen, Project Officer - MRI contract 68-02-4252

Cindy Stroup, Project Officer - Battelle contract 68-02-4243

**16. Abstract (Limit: 200 words)**


This report presents the results of two field studies conducted in 1986 by the Environmental Protection Agency's Office of Toxic Substances (EPA/OTS) under the existing chemicals program to screen selected waterbodies for the presence of chlorinated paraffins. Chlorinated paraffins are saturated straight-chain hydrocarbons ranging from 10 to 30 carbons in length and containing 20 to 70% chlorine by weight. The information gained from these field studies will be coupled with that from other environmental hazard and environmental exposure studies and collectively contribute to an EPA risk assessment for this chemical.

The report also develops an analytical method for chlorinated paraffins in different environmental matrices and includes a rigorous statistical analysis of the data used to validate the method.


**17. Document Analysis a. Descriptors**

Chlorinated Paraffins, lubricating oils, survey design, HRGC/NCIMS/SIM analytic method, statistical assessment of method validation studies.

**b. Identifiers/Open-Ended Terms**

| | |
|---|---|
| Literature review | Chromatography |
| Extraction | Cleanup |
| Mass spectrometry | Statistical analysis |

**c. COSATI Field/Group**

| 18. Availability Statement | 19. Security Class (This Report) | 21. No. of Pages |
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